P - N MOTIFS IN POLYMERS AND RINGS. PHOSPHAZENE PENDANT POLYMERS AND AMINOSUBSTITUTED POLYPHOSPHAZENES

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by

K. VIVEKANANDAN

to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
June, 1997

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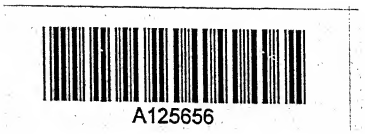

Dedicated to

My Parents

CERTIFICATE

It is certified that the work contained in this thesis entitled *P - N MOTIFS IN POLYMERS AND RINGS. PHOSPHAZENE PENDANT POLYMERS AND AMINOSUBSTITUTED POLYPHOSPHAZENES* by *K. VIVEKANANDAN* has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

Professor V. CHANDRASEKHAR
Department of Chemistry
Indian Institute of Technology
Kanpur

June, 1997

STATEMENT

I hereby declare that the matter embodied in this thesis , "**P-N Motifs in Polymers and Rings. Phosphazene Pendant Polymers and Amino Substituted Polyphosphazenes**", is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India under the supervison of **Prof. V. Chandrasekhar.**

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made whereever the work described is based on the findings of other investigators.

Kanpur
June, 1997

(K. Vivekanandan)

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR, INDIA

CERTIFICATE OF COURSE WORK

This is to certify that **K. VIVEKANANDAN** has satisfactorily completed all the courses required for the Ph.D degree. The courses include:

CHM 605	Principles of Organic Chemistry
CHM 625	Principles of Physical Chemistry
CHM 645	Principles of Inorganic Chemistry
CHM 664	Modern Physical Methods in Chemistry
CHM 646	Bio-Inorganic Chemistry
CHM 632	Enzyme Kinetics and Mechanisms
CHM 800	General Seminar
CHM 801	Special Seminar
CHM 900	Post-graduate Research

K. Vivekanandan was admitted to the candidacy of the Ph.D degree in September 1993 after he successfully completed the written and oral qualifying examinations.

(Prof. S. K. Dogra)
Head
Department of Chemistry
I.I.T. Kanpur

(Prof. T. K. Chandrasekhar)
Convenor, DPGC
Department of Chemistry
I.I.T.Kanpur

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(K. Vivekanandan)

Synopsis

This thesis contains four chapters.

Chapter 1 gives an over all review on cyclophosphazenes and polyphosphazenes. Substitution reactions of chlorocyclophosphazenes by amines and the reaction mechanisms involved have been discussed. The coordination and organometallic chemistry of various cyclophosphazene ligands is also presented. The various synthetic routes involved in the preparation of polyphosphazenes are described. The structural aspects of these polymers along with some of the structure-property relationship involved are also discussed.

Chapter 2 deals with the reaction of the cyclic amines, cyclopropylamine, cyclopentylamine and cyclohexylamine with $N_3P_3Cl_6$, $N_4P_4Cl_8$ and $[NPCl_2]_n$. In the reactions with $N_3P_3Cl_6$ only trace amounts of the hexakis product $N_3P_3(NHR)_6$ have been isolated, where as the predominant product in the reactions with $N_3P_3Cl_6$ and an excess of RNH_2 is the gem-tetrakis derivative $N_3P_3Cl_2(NHR)_4$. These derivatives have been characterized by multinuclear NMR and FAB mass. Single crystal x-ray structural analysis of $N_3P_3Cl_2(NHR)_4$ (R = Cyclohexylamine) and $N_4P_4R_8$ (R = cyclopropylamine) have also been carried out. While the six membered ring is more planar and the eight membered ring is highly puckered :

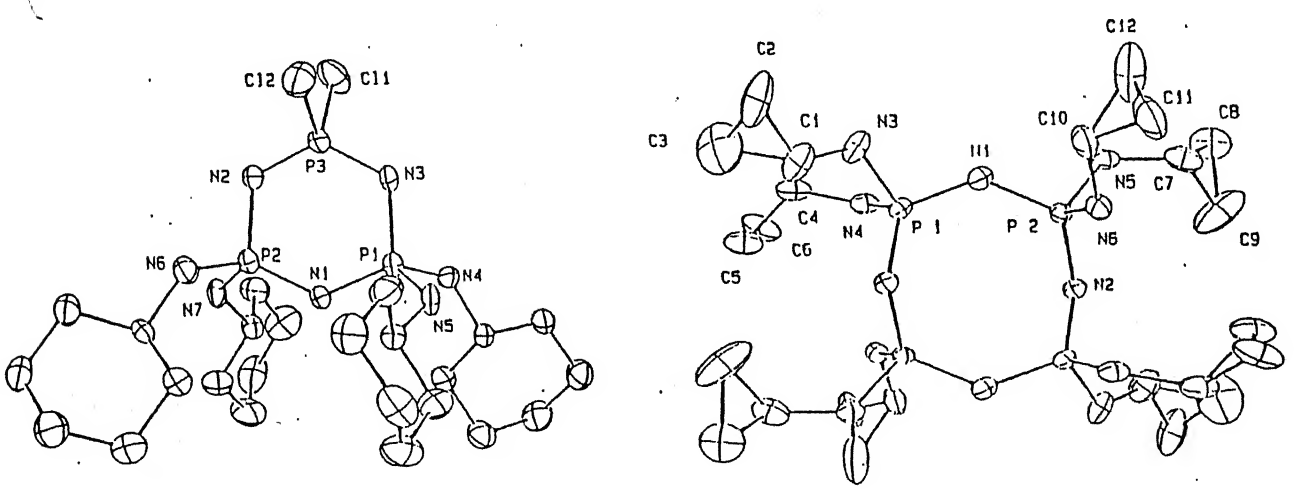


Figure 1: ORTEP Plots of DCHEA and OCPRA.

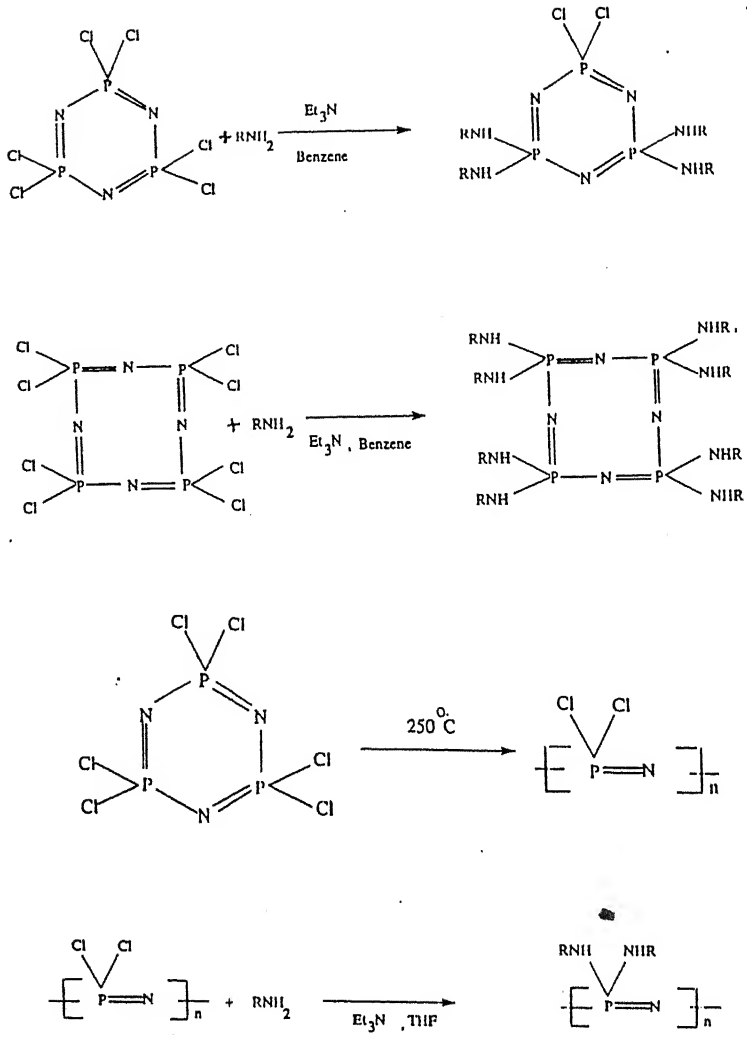


Figure 2: Synthetic Strategies for Preparing Cyclic Amino Polyphosphazenes.

Polyphosphazenes containing cyclic amino substituents $[NP(NHR)_2]_n$ (R = cyclopropylamine, cyclopentylamine, cyclohexylamine) have been synthesized and characterized by viscosity measurement, thermal analysis, powder x-ray diffraction, and multinuclear NMR. All the polymers are high molecular weght materials and are amorphous with only a short range microcrystallinity as shown by powder x-ray diffraction studies. These polymers have high glass transition temperatures and undergo multistep thermal decomposition processes with a char yield of 35 - 40% at 650 °C.

Chapter 3 describes the synthesis of cyclotetraphosphazene linked organic monomers:

The structural characterization of these monomers by multi nuclear NMR, FAB mass and other spectroscopic methods has been carried out and forms part of this chapter. Attempts to homopolymerize these monomers and the properties of the new homopolymer derived from ($N_4P_4Cl_7OC_{14}H_{11}$) are also described. Some copolymers derived from the above monomer have also been synthesized and form part of this chapter. The homopolymer, as well as the copolymers are highly flame retardant.

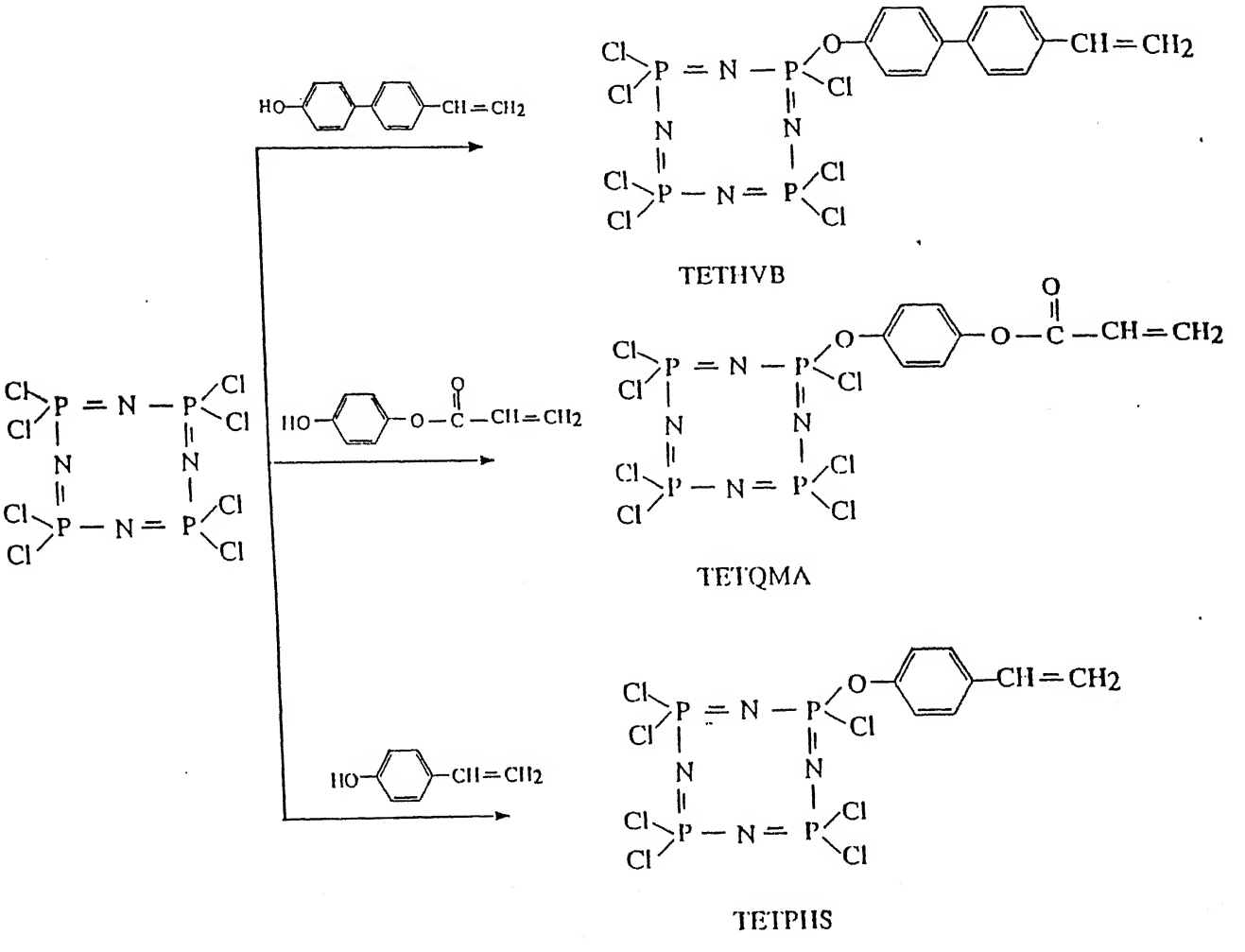


Figure 3: Synthetic Route Involved in the Preparation of TETHVB, TETQMA and TETPHS.

Chapter 4 discusses the synthesis of pendant pyrazolylcyclophosphazenes. The monomers and the polymers have been characterized by multinuclear NMR and other analytical techniques. These have been studied for their interaction with transition metals such as copper halides. Model compound studies have also been carried out. These include an x-ray structure of $N_3P_3(Pz)_6$:

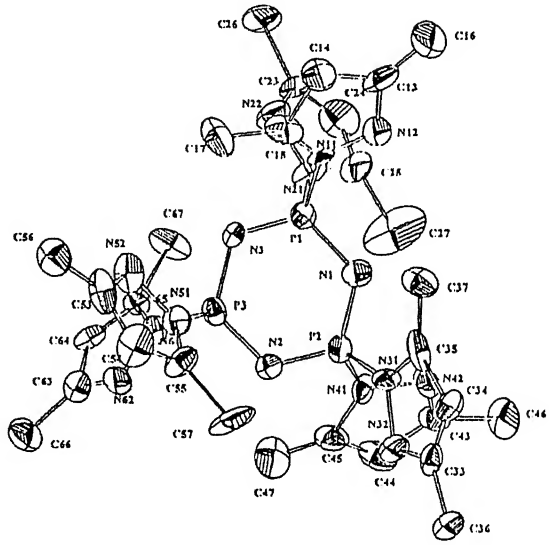


Figure 4: ORTEP Plot of $N_3P_3(Pz)_6$.

The synthesis of $N_3P_3(NH_2)_2(Pz)_4$ and the x-ray structure of $N_3P_3(NH_2)_2(Pz)_4.CoCl_2$ also forms part of this chapter.

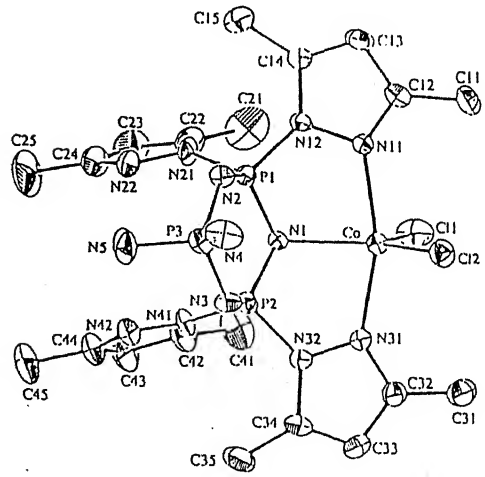
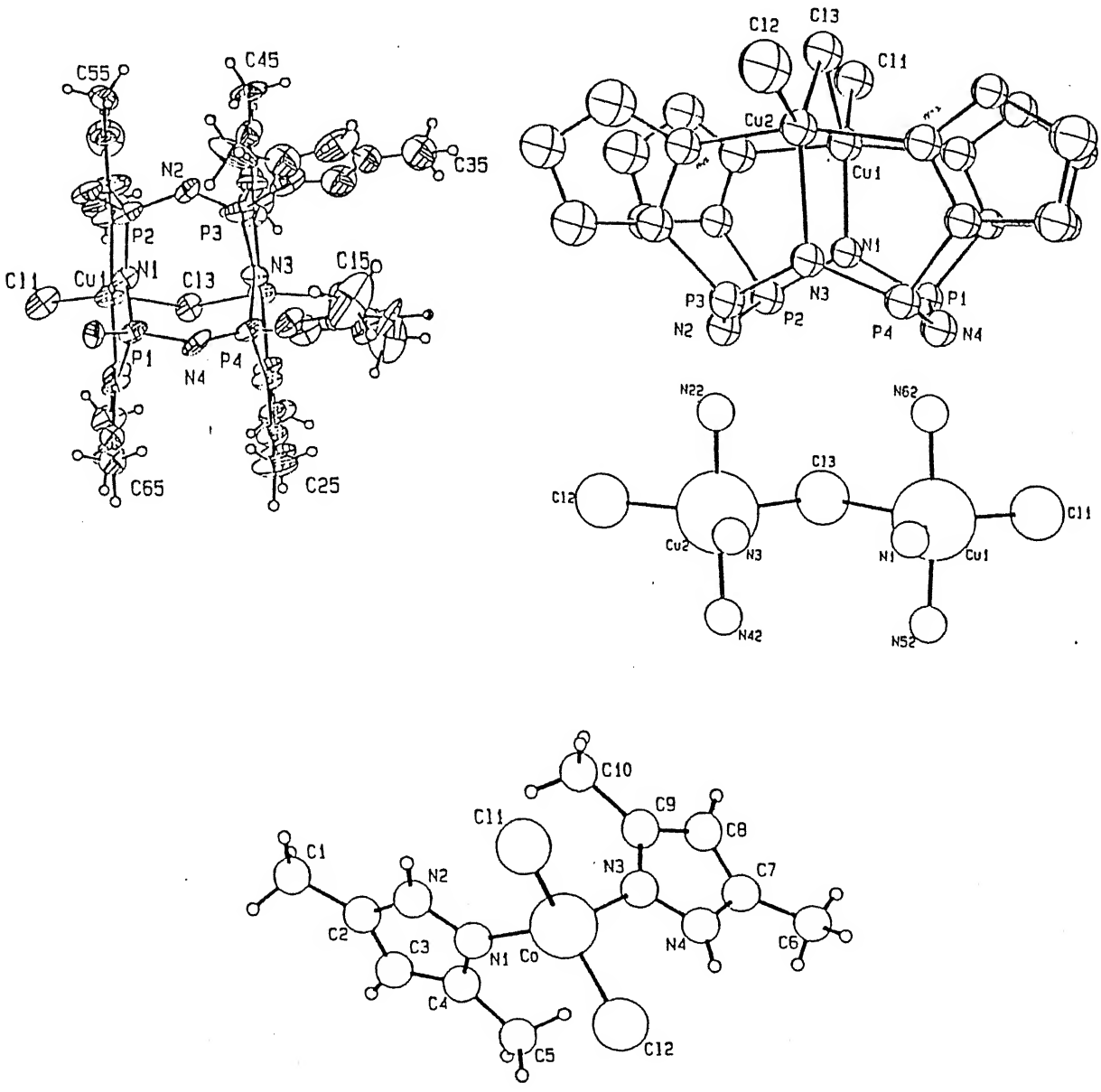


Figure 5: Molecular Structure of DIAMPZ.$CoCl_2$

Attempts to isolate the $CoCl_2$ complex of $N_4P_4(Pz)_8$ have resulted in the hydrolysis of the ring and in the isolation of $(Pz)_2CoCl_2$. A novel partially hydrolyzed pyrozolyl-cyclotetraphosphazene derivative containing binuclear copper centres has also been structurally characterized.



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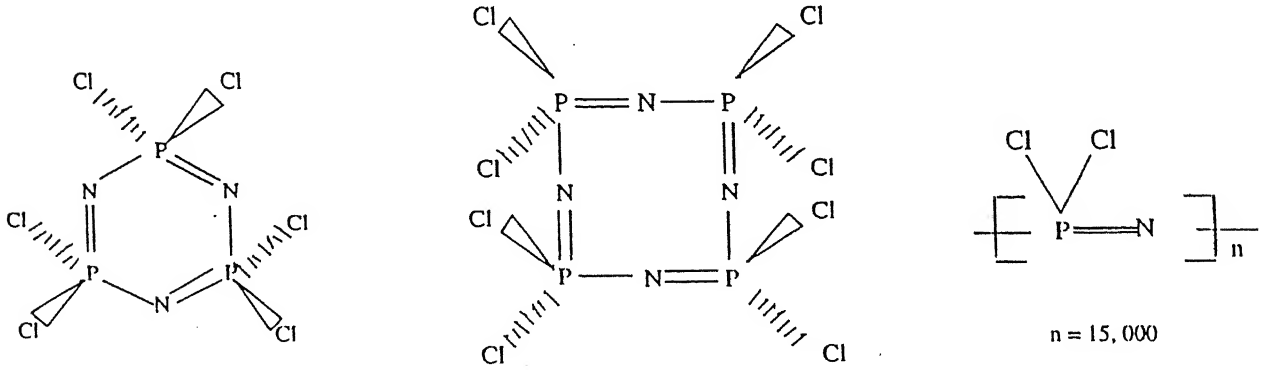
Chapter 1

Introduction

1.1 General Features

Cyclophosphazenes are inorganic ring systems with alternating phosphorus and nitrogen atoms in the frame work [1,2]. Phosphorus is pentavalent and tetra coordinate, while nitrogen is trivalent and di coordinate. While phosphorus has two exocyclic substituents nitrogen has none. Representative examples of this class of compounds are shown in Figure 1.1.



Hexachlorocyclotriphosphazene Octachlorocyclotetraphosphazene Polydichlorophosphazene

Figure 1.1: Representative Examples of Phosphazene Compounds.

Interest in the study of these inorganic ring systems stems from several reasons. The nucleophilic substitution reactions of the precursor compounds hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ and octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ have been studied with a wide range of nucleophilic reagents such as amines, alcohols phenols, and organometallic reagents etc [3].

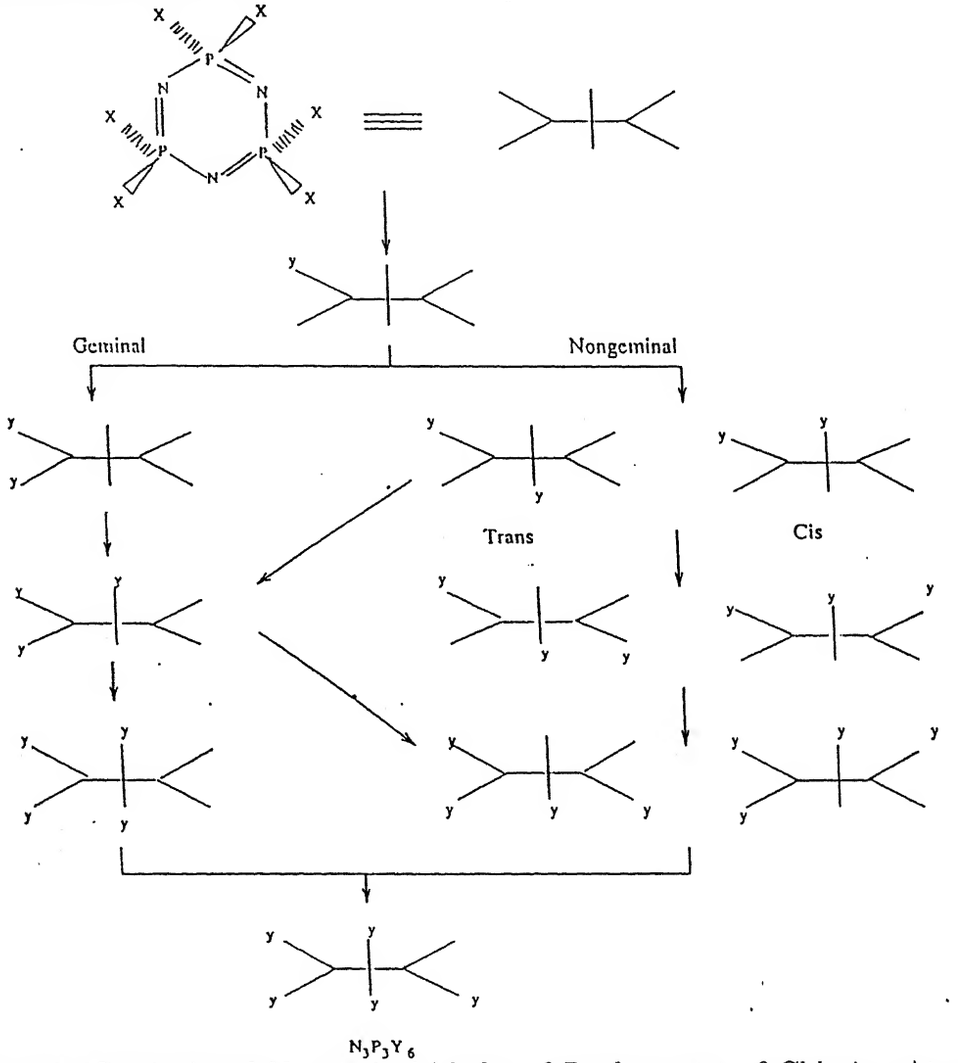


Figure 1.2: Geminal and Nongeminal Modes of Replacement of Chlorine Atoms from $N_3P_3Cl_6$.

The studies with the six membered trimeric system $N_3P_3Cl_6$ have been more exhaustive [4]. All of these studies indicate interesting stereo and regio selective preferences. The possible substitution routes for $N_3P_3Cl_6$ and $N_4P_4Cl_8$ are summarized in Figures 1.2 and 1.3 respectively. A recent review summarizes the progress of work on these aspects [5].

Another reason for the interest in the study of cyclophosphazenes is the possible utilization of these rings as coordinating ligands [6-11]. While the chloro derivatives themselves are not very good ligands, suitably substituted cyclophosphazenes have been found to interact with transition metals to afford a variety of novel complexes . Figure 1.4 shows some of the representative types of transition metal complexes isolated using cyclophosphazenes as ligands.

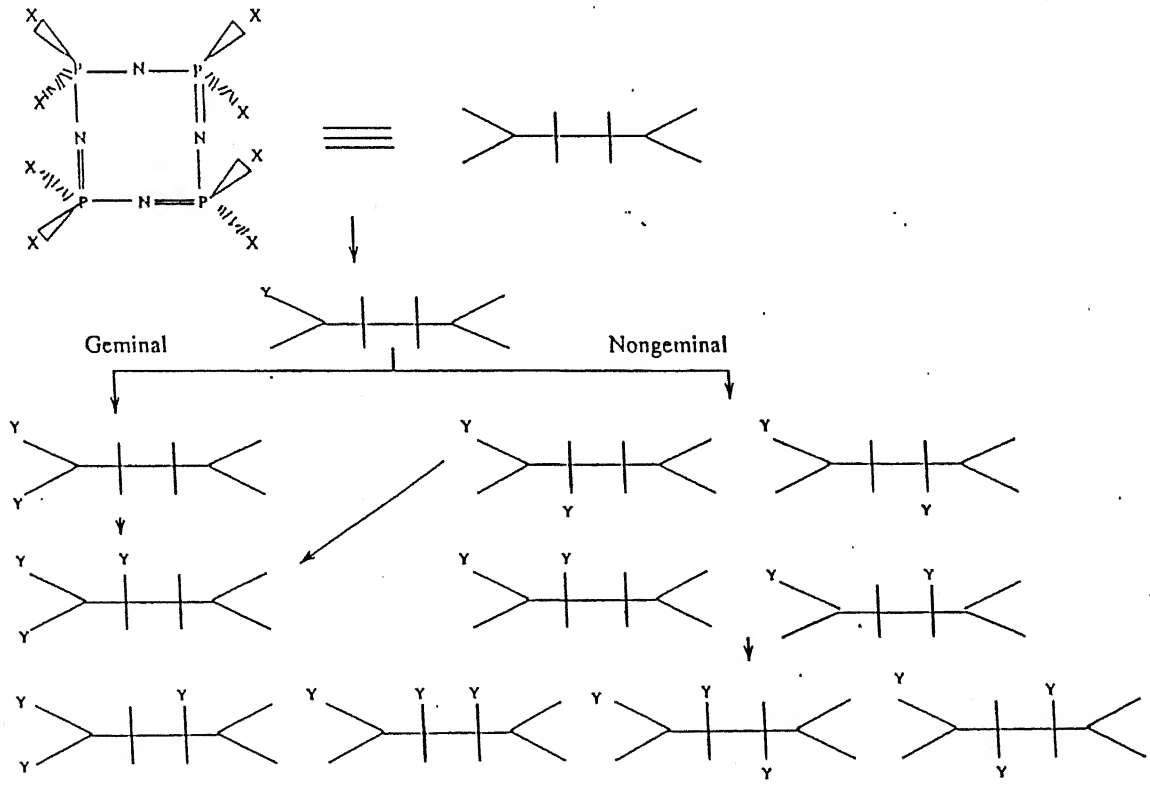


Figure 1.3: Possible Substitution Products from $N_4P_4Cl_8$.

In addition to the above reasons, another important aspect which has attracted attention is the ring opening polymerization of chlorocyclophosphazenes to poly[dichlorop phazene] [12](Figure 1.5).

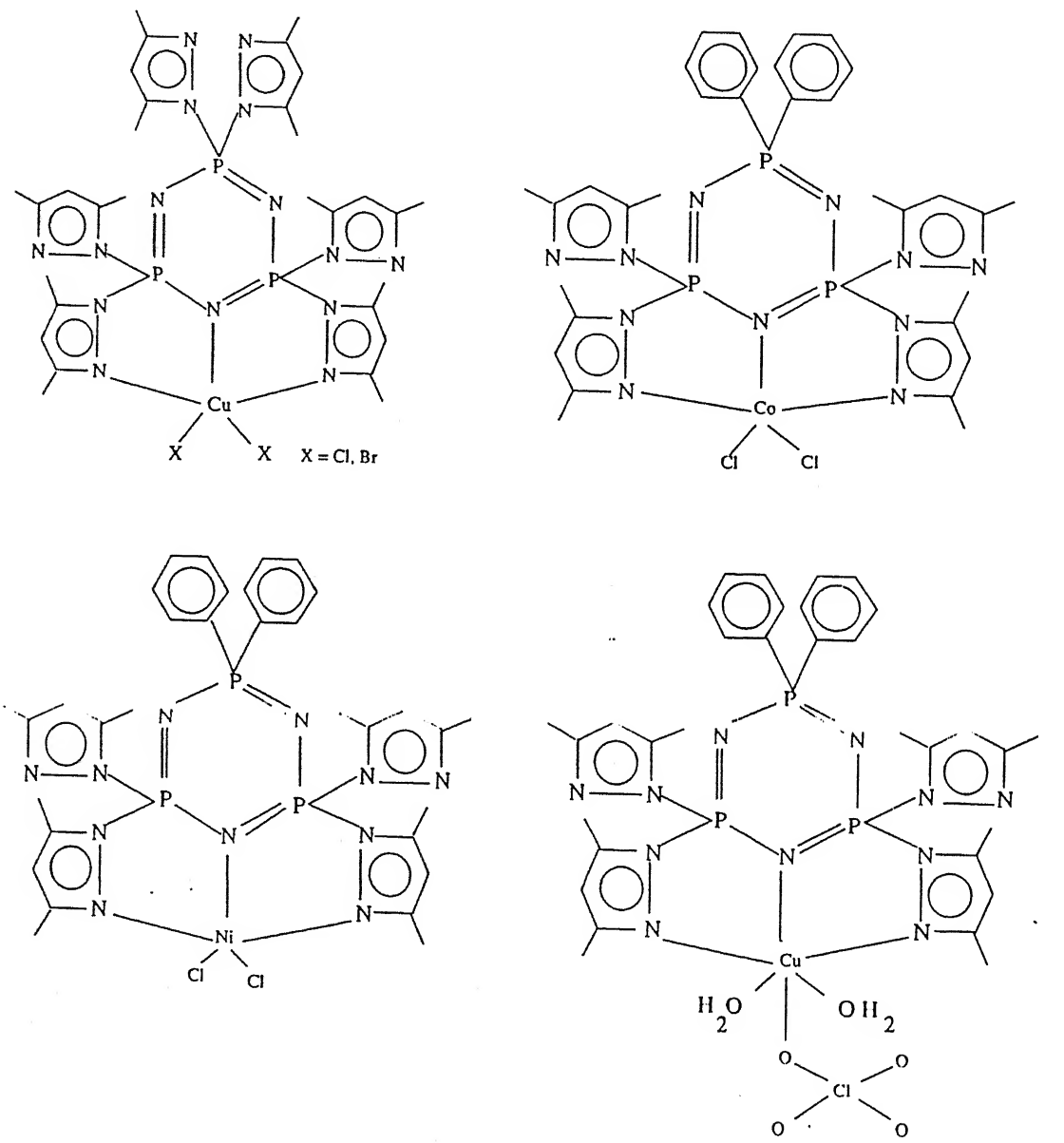


Figure 1.4: Representative Transition Metal Complexes of Cyclophosphazenes.

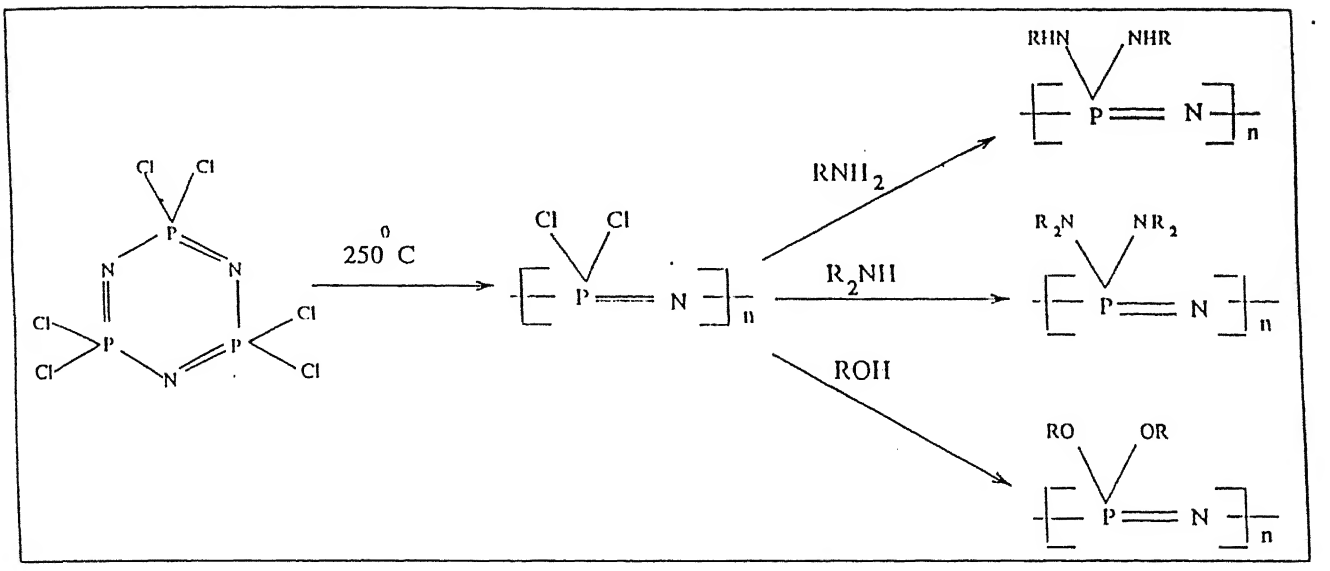


Figure 1.5: Synthetic Route for Preparing Polyphosphazenes.

The poly[dichlorophosphazene] itself, although a very high molecular material, is not useful because of the ready hydrolysis of the P - Cl bonds [13-15]. However, this reactivity of the P - Cl bonds can be taken advantage of in macromolecular substitution reactions involving replacing of the chlorines by a wide variety of substituents. This route apart from affording hydrolytically stable polymers also provides a convenient way to increase the polymer architechture and diversity. Thus more than three hundred different types of polyphosphazenes have been prepared utilizing the above protocol [16-17]. Although other methods of polyphosphazene assembly are now known, as discussed *vide infra*, these give rise to specific types of polymers, in contrast to the general ring opening route.

In the following account a description of the above aspects of cyclophosphazene and polyphosphazene chemistry are presented that is relevant to the theme of study in this thesis.

1.2 Cyclophosphazenes

1.2.1 Bonding Aspects of Cyclophosphazenes

The basic σ frame work of the ring system is constituted from the sp^3 hybrid orbitals of phosphorus and approximately sp^2 orbitals of nitrogen. Two sp^2 orbitals of nitrogen are involved in bonding to phosphorus while the third which is inplane with the P - N - P segment is occupied by a lone pair. The remaining odd electron on nitrogen resides in a p_z orbital which is perpendicular to the plane of the ring, while the one on phosphorus is present on any appropriate orbital such as 3d, 4s, 4p or their combinations. Three types of π bonding situations have been envisaged [18] (Figure 1.6).

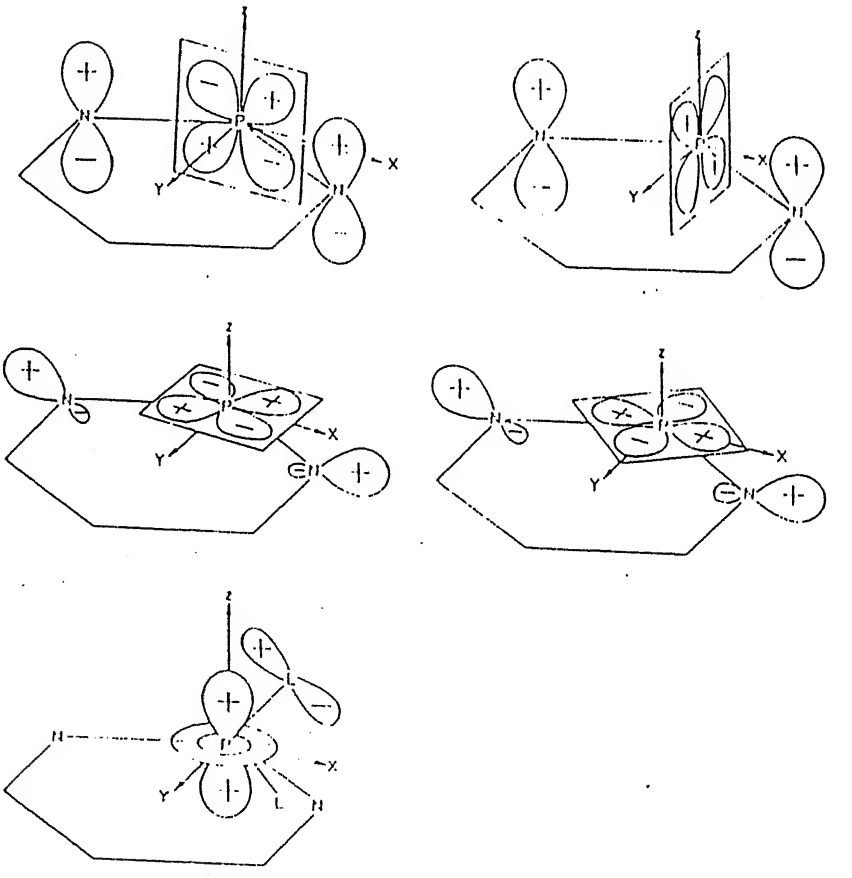


Figure 1.6: Types of II Bonding in Cyclophosphazenes.

1. A combination of the odd electrons on nitrogen and phosphorus to give a π_a bonding (antisymmetric to the P - N - P plane).

2. A combination of the inplane sp^2 orbital of nitrogen and an appropriate d orbital such as $d_{x^2-y^2}$ or d_{xy} to give a π_s bonding (symmetric to the P - N - P plane).

3. A π bonding between phosphorus and the exocyclic substituent involving conjugate electron release from the substituent lonepair into a phosphorus d orbital.

The major contribution to the ring π bonding seems to be of the π_a type. A distinction has been made by Craig and Paddock in the π_a type [19]: if d_{xz} orbitals are involved exclusively from phosphorus it leads to a delocalized bonding with alternate signs around the ring (heteromorphic), while if d_{yz} are used exclusively it leads to constant signs of interaction (homomorphic). Dewar has suggested [20] equal contribution from d_{xz} and d_{yz} orbitals resulting in the π_a system to be localised over a three bond P - N - P segment. It has been shown that both these approaches converge to the same result. Some amount of transannular phosphorus-phosphorus bonding has also been suggested. Several x-ray structures of cyclophosphazenes have been completed and the results correlated with the bonding models discussed above. The important results are:

(a) In homogeneously persubstituted cyclophosphazenes $N_3P_3R_6$, bond distances are virtually equal with in the molecule with the endocyclic P - N bondlengths being 1.55 Å to 1.61 Å which are shorter than normal P - N single bond distance (1.77 Å) and reflect the multiple bond character between phosphorus and nitrogen.

(b) For a heterogeneously substituted compound the ring P - N bond lengths are not equal. For mono and geminal di and tetra substituted phosphazenes $N_3P_3XX'Y_4$

there exists three pairs of P - N bonds, a, b, c. When X = X'= an organic group or X = substitutent and X' = halogen (Y = halogen) the P - N bond lengths are in the following order $a > c > b$. In geminal tetrasubstituted compounds where Y = organic group and X and X' = halogen the P - N bond lengths are in the order $b > c > a$ (Figure 1.7).

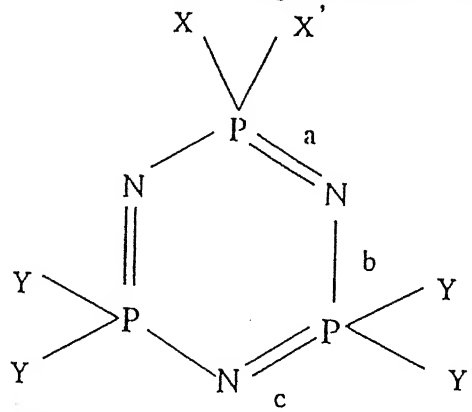


Figure 1.7: Three Different Types of P-N Bondlengths.

These bond length differences are due to different degrees of ring π bonding with in a molecule. Strong electronegative substituents contract the d orbital at phosphorus and make them more amenable for π bonding with ring nitrogens, thus decreasing the affected P - N bond length.

(c) Ring conformation of cyclic six membered rings are planar or slightly puckered while the eight membered rings are generally highly flexible and puckered, with $N_4P_4Cl_8$ it self crystallizing in two different conformations [21] a boat (K - form) and a chair (T - form). It appears that the energy differences between the various ring conformations in the eight membered rings are small and the Predominance of a particular conformation is as a result of a number of intra and intermolecular factors such as orientation of substituents, steric and electronic nature of substituents, crystal packing effects, hydrogen bonding interactions etc.

1.2.2 Nucleophilic Substitution Reactions of Chlorocyclo phosphazenes Involving Amines

Although several nucleophilic substitution reactions with $N_3P_3Cl_6$ and $N_4P_4Cl_8$ are known with reagents such as amines, alcohols, organometallic reagents etc., only a brief summary of the reactions with amines is given below. Excellent reviews and monographs are available that deal in detail with the nucleophilic substitution reactions of chlorocyclophosphazenes [3-5,22].

1.2.3 Reactions of $N_3P_3X_6$

The hexahalocyclotriphosphazenes, $N_3P_3X_6$ (X = Cl, Br, F) can undergo substitution reactions with amines by cleavage of the P - X bond (*see* Figure 1.5.) This reaction is quite general and reactions are known with several amines. However the data on $N_3P_3F_6$ and $N_3P_3Br_6$ are scarce . While in the case of $N_3P_3F_6$ the reactions with amines are very slow owing to the decreased lability of the P - F bond (which may due to a strong $d_\pi - p_\pi$ bonding between F and P) in case of $N_3P_3Br_6$ the difficulty may be due to the tedious synthesis of $N_3P_3Br_6$. Recently Shreeve and coworkers have shown that a reaction with $N_3P_3F_6$ with silyl substituted reagents are quite facile [23,24]. The general trends of the aminolysis reactions of $N_3P_3Cl_6$ can be summarized as follows:

1. Reactions with primary amines is complex. While amines such as ammonia and t-butyl amine react in a geminal manner [25], with other amines a nongeminal pathway is preferred. Also while ethyl amine affords nongeminal products [26,27], β-halo ethyl amines give geminal products [28,29].

2. Reactions with secondary amines afford mainly nongeminal products, with the exception of aziridine [30,31].

3. Solvent effects are extremely important, although poorly understood, in deter-

mining the stereo and regio control of substitution [4,32]. Recent kinetic investigations on several systems suggests the presence of different types of mechanistic pathways operating in the substitution reactions [33-39].

A proton abstraction mechanism [26] proposed by Shaw envisages the formation of a three coordinate intermediate *via* the expulsion of HCl (Figure 1.8). The need to relieve steric strain in this intermediate leads to formation of geminal products. Recent work by Krishnamurthy in trapping the tricoordinate phosphorus reactive intermediate lends credance to this mechanism [37].

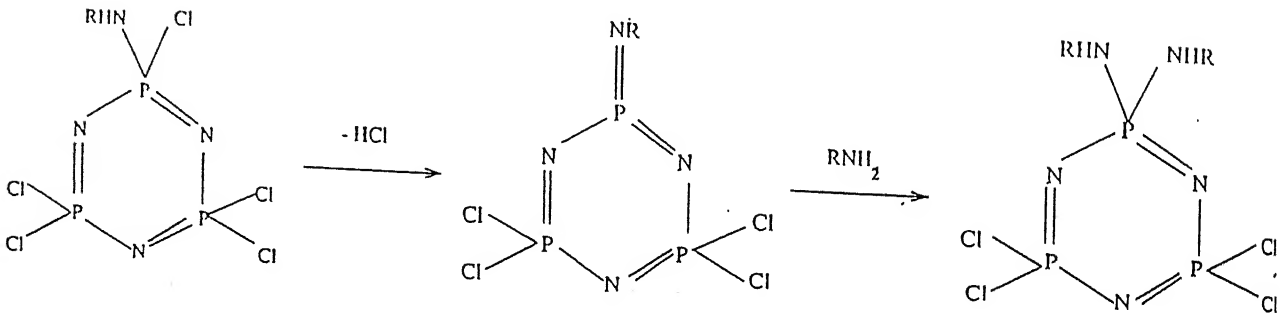


Figure 1.8: Proton Abstraction Mechanism.

Formation of nongeminal products at the bis stage is explained by steric as well as electronic grounds. Thus the presence of a NHR (an electron releasing substituent) increases the electron density on phosphorus and deactivates this centre for nucleophilic substitution (Figure 1.9).

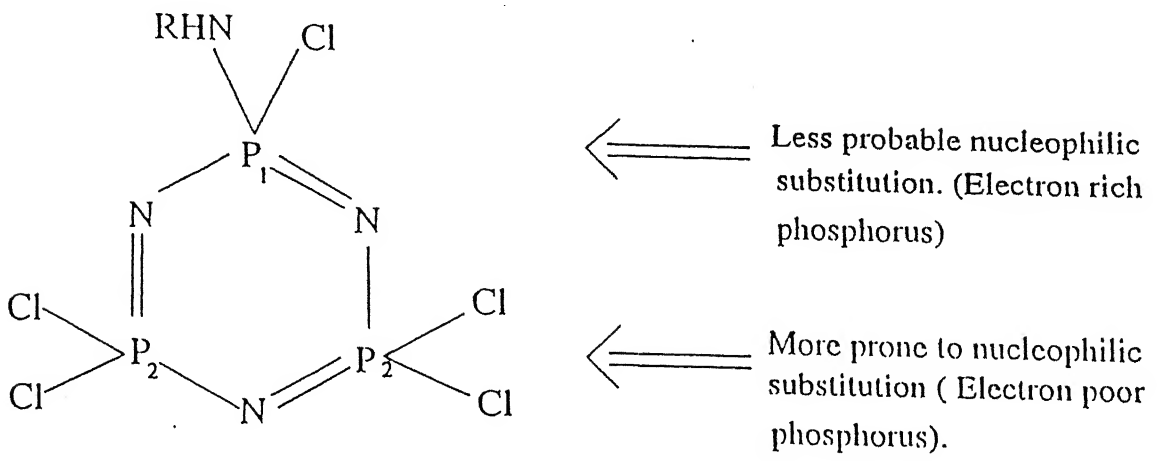


Figure 1.9: Formation of Non-geminal Products.

Secondly P(1) is more crowded for a five coordinate S_N2 transition state than P(2). In this context it must be mentioned that kinetic evidence suggests the presence of two types S_N2 mechanisms (a) formation of a neutral five coordinate phosphorus intermediate followed by the expulsion of the leaving group (b) A concerted S_N2 mechanism such as that known in carbon systems.

In addition, evidence for the operation of a S_N1 mechanism has been found in the conversion of $2,4,6-trans-N_3P_3Cl_3(NMe_2)_3$ to $2,2,4,6$ cis $N_3P_3Cl_2(NMe_2)_4$ and in the conversion of $N_3P_3(OPh)_5Cl$ to $N_3P_3(OPh)_5(NMe_2)$ [40,41]. Steric crowding at the phosphorus centres combined with the total electron release of the other substituents causes the preference for a dissociate S_N1 mechanism (Figure 1.10).

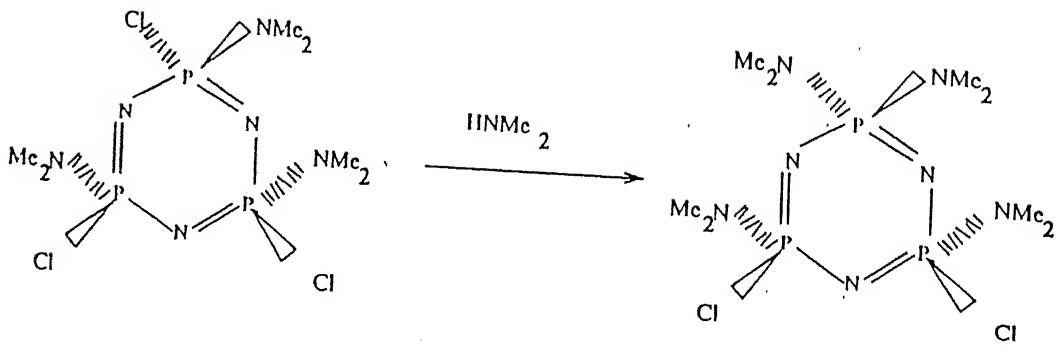


Figure 1.10: Example for a Dissociate S_N1 Mechanism.

1.2.4 Reactions of $N_4P_4Cl_8$ with Amines

The reactions of $N_4P_4Cl_8$ with amines are much faster ($\sim$ 200 times) than $N_3P_3Cl_6$ presumably due to the greater torsional mobility of the former allowing for an easy structural reorganization required for the S_N2 transition state. Thus only nongeminal substitution is found with $N_4P_4Cl_8$.

In addition to 'normal' products, unusual bicyclic products have been isolated [39]. Thus the reaction of 2,6-trans $N_4P_4Cl_6(NHEt)_2$ with dimethyl amine in ether affords a 'normal' product $N_4P_4(NMe_2)_6(NHEt)_2$ while in chloroform the reaction gives a bicyclic derivative. This reaction has been found to be general and its mechanism has been elucidated. (*see* Figure 1.11)[42].

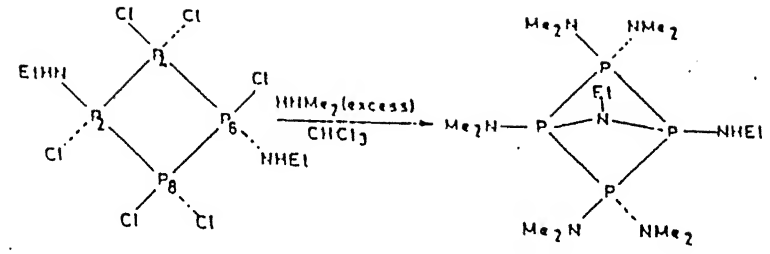


Figure 1.11: Formation of Bicyclic Products.

1.3 Metal Complexes of Cyclophosphazenes

This aspect has recently been reviewed [5]. There are atleast four ways of interaction of phosphazenes with transition metals. These are (a) skeletal nitrogen coordination, (b) ionic salt type interaction. (c) ring phosphorus interaction (d) exocyclic group participation.

1.3.1 Skeletal Nitrogen Coordination

Each skeletal nitrogen atom of a phosphazene bears a lone pair of electrons and therefore, phosphazenes can be used as classical ligands. However, the availability of lone pair of electrons for donation to metals depends on the substituents on phosphorus. Electron-withdrawing side groups, such as flourine or trifluoroethoxy, reduce the basicity of skeletal nitrogen but, at the same time, strengthen the skeletal bonds. Conversely, electron-releasing substituents such as alkyamino, alkyl etc., enhance the basicity of the skeletal nitrogen atoms. An additional feature that governs the ligating behaviour of cyclophosphazene is the ring size. Thus, larger sized rings which are puckered can easily accomodate the metals in their preferential coordination geometries.

Although cyclotriphosphazene possess three nitrogen donors, no case has been reported in which two or three nitrogens engage simultaneously in coordination. Thus $N_3P_3(CH_3)_6$ interacts with titanium tetrachloride in an unidentate fashion [43]. Amino phosphazenes such as $N_3P_3(NHPr^n)_6$ and $N_3P_3(NHBu^n)_6$ were reported to form complexes with cobalt, copper and nickel halides [44]. However, the structures of these have not been established as no crystal structures are available.

Cyclotetraphosphazenes behave both as monodentate and bidentate ligands in the favorable circumstances i.e., depending upon the nature of the metal. Thus, $N_4P_4(CH_3)_8$ reacts with anhydrous cupric chloride in methyl ethyl ketone, to result in a complex in which copper is bonded to a ring nitrogen; in this complex cyclotetraphosphazene functions as an unidentate ligand [45] (Figure 1.12). An antipodal nitrogen is found protonated in this complex. But an analogous reaction of $N_4P_4(CH_3)_8$ with $PtCl_2$ results in a square planar complex, with the two opposite ring nitrogen atoms coordinated to platinum in a cis manner (Figure 1.12) [46]. A complex of similar structure has been isolated in the reaction of $N_4P_4(NHMe)_8$ with K_2PtCl_4 in presence of 18-crown-6 [47]. In these complexes cyclotetraphosphazenes coordinate in a bidentate manner.

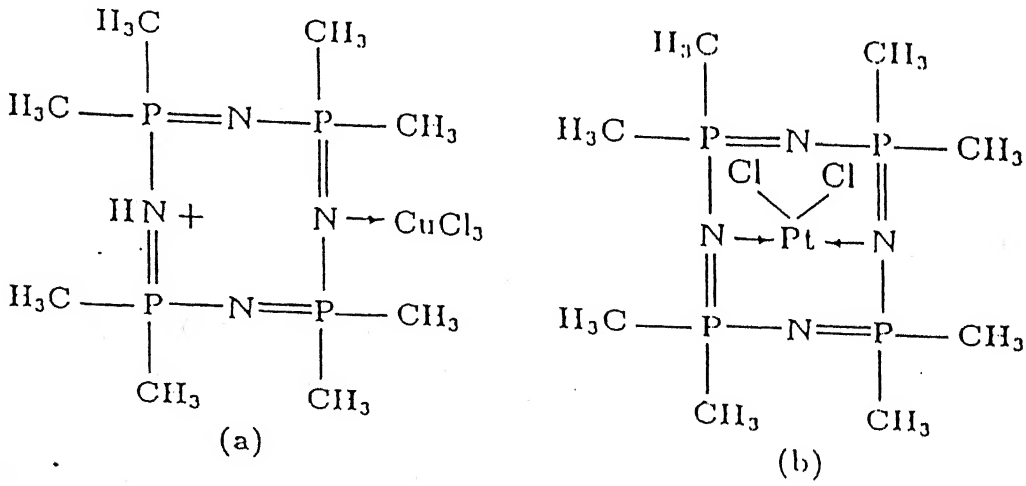


Figure 1.12: Examples of Ring Nitrogen Coordination of Cyclotetraphosphazenes.

With higher membered ring systems such as $N_6P_6(NMe_2)_{12}$, $N_6P_6(CH_3)_{12}$ and $N_8P_8(CH_3)_{16}$ coordination of two or four skeletal nitrogen atoms is observed [48-53]. The twelve membered ring compound $N_6P_6(CH_3)_{12}$ forms 1:1 complexes with $PdCl_2$ and $PtCl_2$. Two ring nitrogen atoms coordinate to the metal and occupy cis positions in the square planar complex [52]. This type of complexation results in six and ten membered chelate rings (Figure 1.13). $N_6P_6(NMe_2)_{12}$ forms complexes of the general formula $[N_6P_6(NMe_2)_{12}].2MCl_2$ (M = Mn, Fe, Co, Cu, Zn) [48]. The crystal structures of cobalt and copper complexes show that the basal site of a distorted square pyramid occupied by four skeletal nitrogen atoms and a chlorine atom at the apical position [49-51]. The structure is unique in that it contains two six-membered and two four membered chelate rings(*Figure*1.13). The nitrate analogs $[N_6P_6(NMe_2)_{12}.M(NO_3)_2]$ (M = Co, Ni, Cu, Mn) are also beleived to have similar structures. $N_8P_8(CH_3)_{16}$ forms a complex with cobalt nitrate, $[N_8P_8(CH_3)_{16}.Co(NO_3)](NO_3)$ in which the cobalt exits in a trigonal prismatic geometry [53]. The metal environment consists of two oxygens from a nitrato group and four skeletal nitrogen atoms of the cyclophosphazene ring.

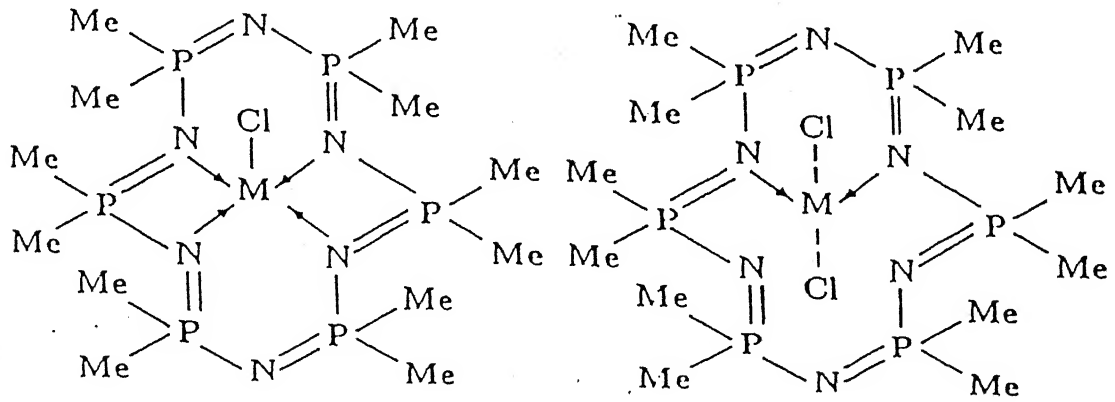


Figure 1.13: Different Coordination Modes of Cyclohexaphosphazenes.

1.3.2 Ionic and Salt-type Species

In aminophosphazenes the amino substituents being electron-donating groups, increase the basicity of the skeletal nitrogen atom. These basic nitrogens can acquire a proton or alkyl cation to generate onium type sites that function as counterions for metallo anionic units. Thus $N_3P_3(NMe_2)_6$ and $N_4P_4(CH_3)_8$ react with $CoCl_2$ to give protonated species $[N_3P_3(NMe_2)_6H^+]_2[CoCl_4^{2-}]$ and $[N_4P_4(CH_3)_8H^+]_2$ $[CoCl_4^{2-}]$ respectively [54-56]. Similarly $N_4P_4(NHMe)_8$ reacts with K_2PtCl_4 in presence of HCl to afford $[N_4P_4(NHMe)_8H_2^{2+}]$ $[PtCl_4^{2}-]$ [49]. A hexamolybdate salt of formula $[N_3P_3(NMe_2)_6H^+]_2$ $[Mo_6\ O_{19}^{2-}]$ was formed when $N_3P_3(NMe_2)_6$ reacted with MoO_3 in water [57]. The methyl iodide quarternary salt of $N_4P_4(CH_3)_8$, $[N_4P_4(CH_3)_9^+]I^-$ reacts with chromium and molybdenum hexacarbonyl to generate the species $[N_4P_4(CH_3)\ _9^+]$ $[M(CO)_5\ I^-]$ (M = Cr or Mo) [58,59]. $N_5P_5(CH_3)_{10}$ on interaction with $CuCl_2$ forms a diprotonated salt $[N_5P_5(CH_3)_{10}H_2^{2+}][CuCl_4^{2-}]$ [60].

1.3.3 Ring Phosphorus Interaction with Metals

Two types of phosphorus interactions with transition metals are observed. (1) covalent (2) coordinate. Cyclophosphazene derivatives which contain direct metal-phosphorus covalent bond are obtained by employing either of the methods enumerated below [61].

1. Nucleophilic substitution reactions of transition metal carbonyl anions with halogenocyclophosphazenes.

2. Reactions of phosphazene anions with metal carbonyl halides.

The first technique is complex and halogen abstraction and skeletal cleavage side reactions occur concurrently.

Allcock and co-workers have found that the reaction of $N_3P_3F_6$ with $NaFeCp(CO)_2$ affords the geminally substituted derivative,$N_3P_3F_4$ $[FeCp\ (CO)_2]_2$ [62-64]. This on

photolysis gives a three membered spirocyclic product containing Fe - Fe bond and a bridging carbonyl group (Figure 1.14) [62].

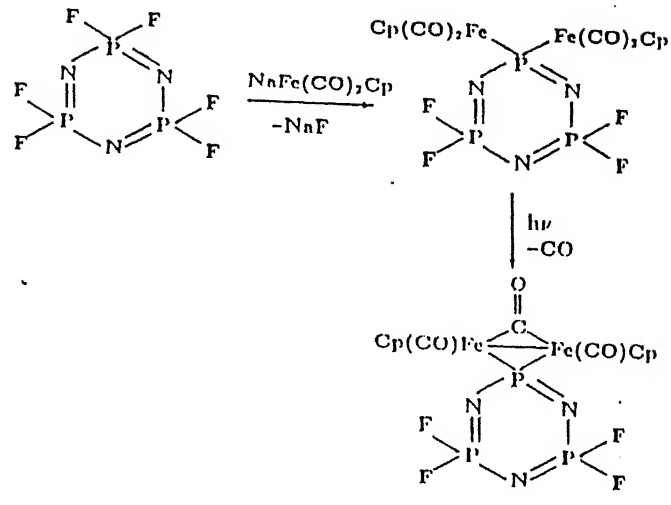


Figure 1.14: Reaction of $N_3P_3F_6$ with $NaFeCp(CO)_2$.

The reaction of $N_3P_3Cl_6$ with disodium octacarbonyldiferrate yields a spiro diiron octacarbonyl bonded phosphazene, 2,2-$N_3P_3Cl_4Fe_2(CO)_8$ and a triiron decacarbonyl bonded phosphazene $N_3P_3Cl_4Fe_3(CO)_{10}$ (Figure 1.15) [65,66]. The latter metallocluster contains both covalent phosphorus - metal and nitrogen - metal coordination bonds, demonstrating both the covalent and coordinative capacities of the cyclophosphazene ring. The diiron derivative acts as a template for the construction of similar dimetal derivatives and clusters with other metals [66,67].

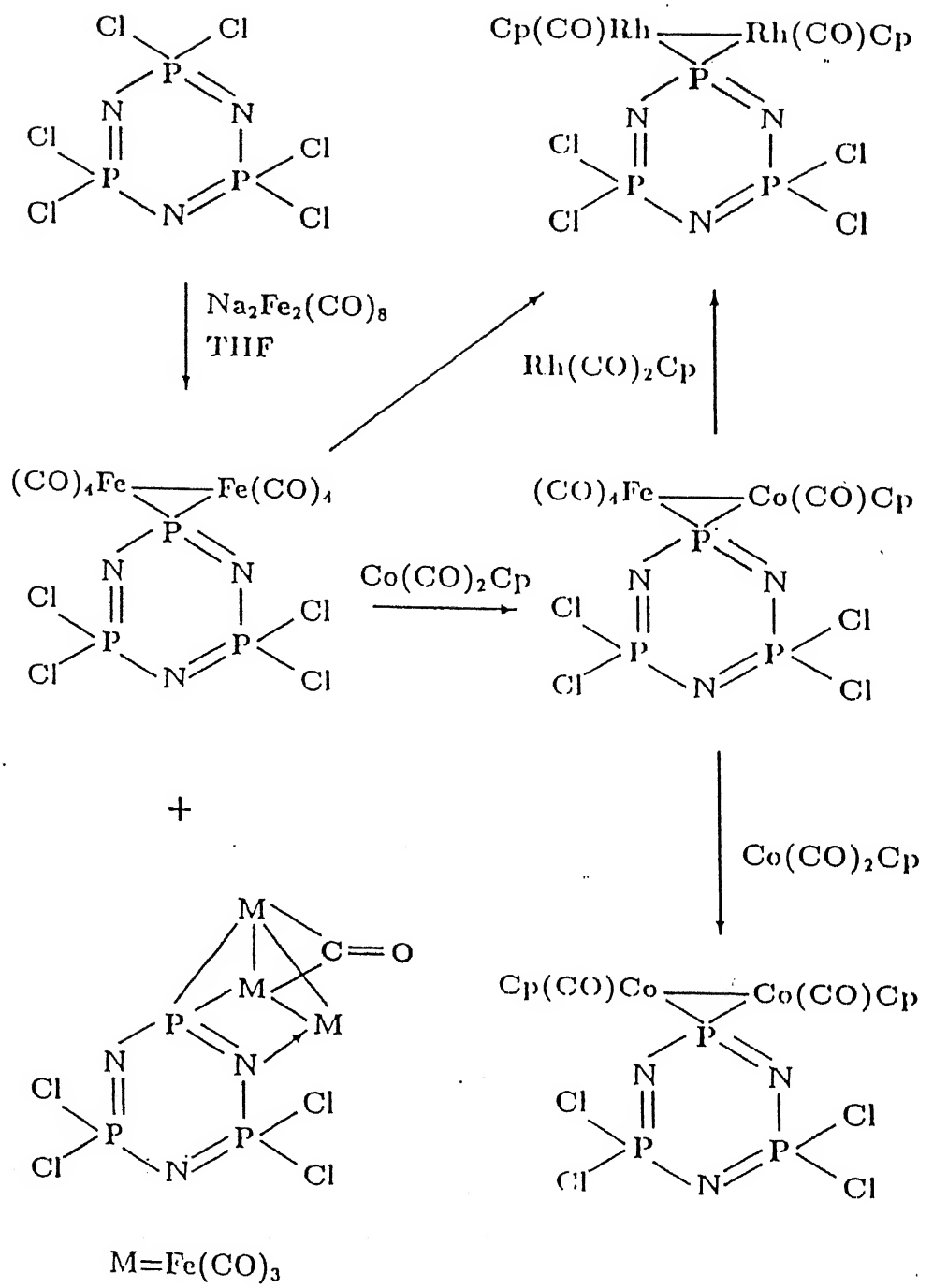


Figure 1.15: Reaction of $N_3P_3Cl_6$ with $Na_2Fe_2(CO)_8$ and Related Reagents.

In another reaction chloride substitution of $N_3P_3Cl_6$ with $[M(CO)_3Cp^-]$ $[n - Bu_4N^+]$ (M = Cr, Mo, W) gives rise to a series of phosphorus metal covalently linked derivatives (Figure 1.16) [68]. With molybdenum and tungsten carbonyl anions an additional chloride displacement also occurs; in the resulting derivative, phosphorus is also linked to a cyclopentadienyl group.

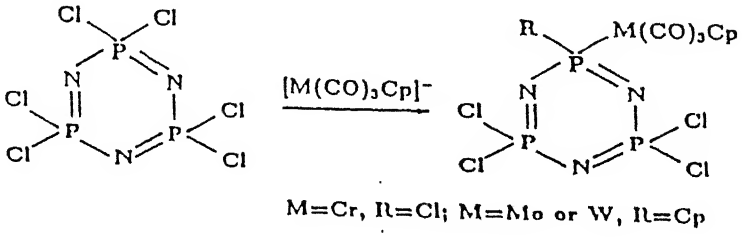


Figure 1.16: Synthesis of Phosphazene-Metal "Covalently Linked" Derivatives.

Atleast three procedures are used to synthesize the phosphazene anions.

1. Hydrido phosphazenes on treatment with alkyl lithium reagents generate the phosphazene anion intermediates [69,70].

2. $LiBEt_3H$ reacts with halogenocyclophosphazenes to produce the same [71].

3. Phosphorus - phosphorus bridged bicyclic phosphazenes are cleaved by $LiBEt_3H$ to result in phosphazene anions [69]. These phosphazene anions on treatment with a metal carbonyl halide, $FeCp(CO)_2I$ gives the desired phosphorus - metal covalently linked derivative (Figure 1.17) [69-71].

Coordination to metal *via* cyclophosphazene phosphorus is not possible as it is pentavalent and has no lone pair of electrons for donation. However, hydrido phosphazenes

containing a P - H bond exist in two resonance forms.

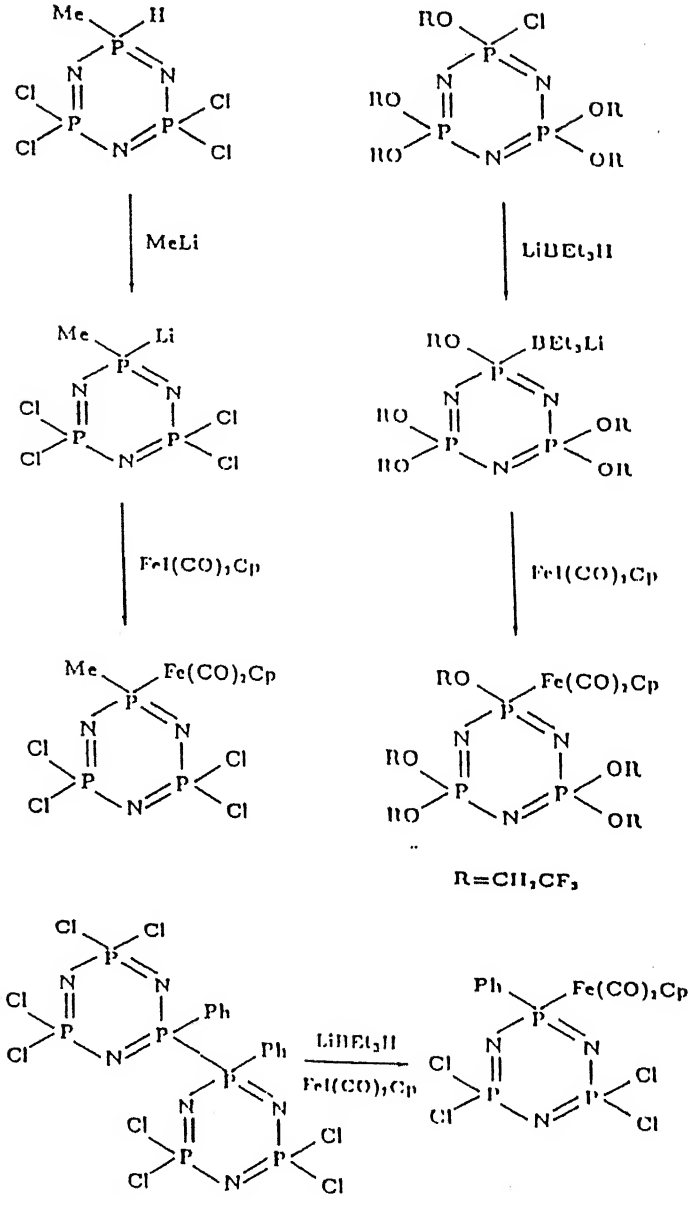
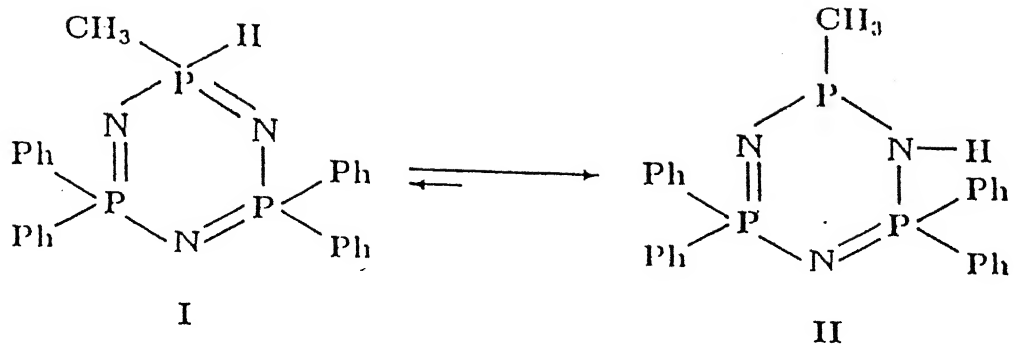


Figure 1.17: Synthesis of Phosphazenes Anions and Their Reaction with $FeCp(CO)_2$.



I II

Figure 1.18: Tautomers of Hydridophosphazenes.

One of these structures (II) contains a trivalent phosphine - like phosphorus which can interact with transition metals. This possibility has been utilized to link the phosphorus atom of the cyclophosphazene ring directly to a metal [72,73]. Thus $N_3P_3Ph_4(CH_3)H$ forms complexes of the type L.M with Au(CO)Cl and $[(CH_3)_2AuCl]_2$ [72]. But with palladium and platinum halides $L_2.M$ type complexes are obtained (Figure 1.19) [73].

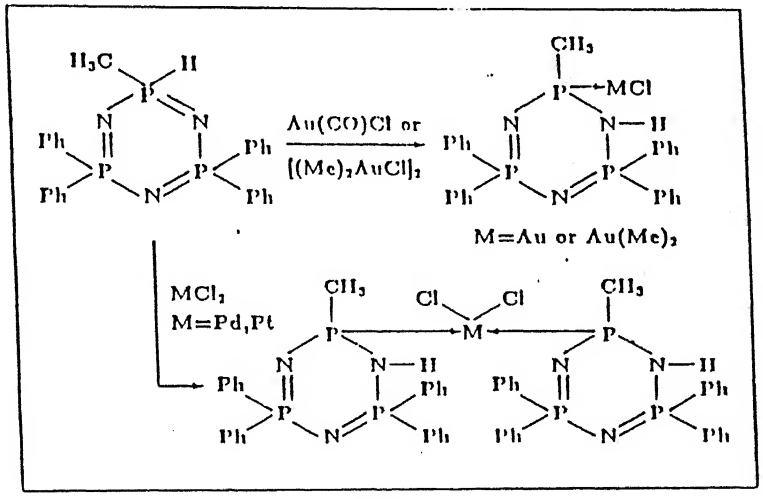


Figure 1.19: Interactions of Hydridophosphazene with Metal Halides.

1.3.4 Exocyclic Group Participation in Coordination

Several complexes have been reported in which the substituents on phosphorus of cyclophosphazene involve in coordination to the metal. In general, two synthetic methodologies are practiced (Figure 1.20)

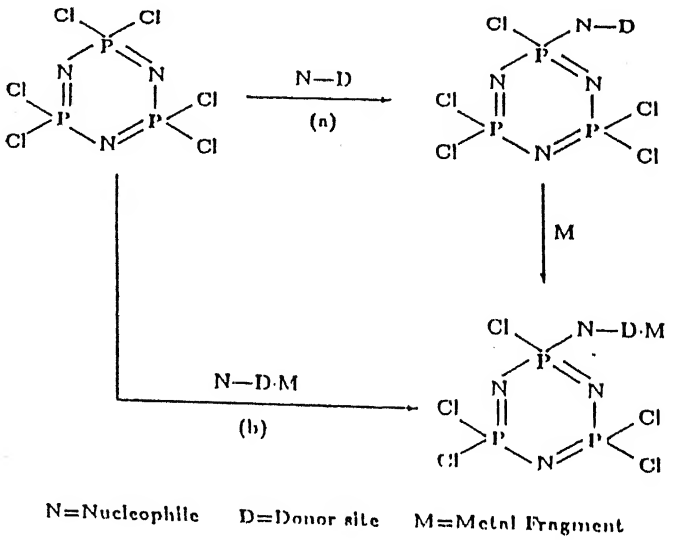


Figure 1.20: Synthetic Stratagies of Exocyclic Group Coordinated Cyclophosphazenes.

(a) A suitable donor group such as alkynes, arenes, schiff bases etc., is incorporated in cyclophosphazene by the usual substitution technique and then treated with metal precursors. (b) In the second synthetic approach, complex containing a reactive functional group on the ligand is subjected to halide displacement reaction with halogenocyclophosphazenes.

For convenience these cyclophosphazene ligands are divided into two categories in keeping with the general practice.

1. π acid ligands and π complexes.

2. Classical ligands.

1.3.5 Π Acid Ligands and Π Complexes

Cyclophosphazene ligands containing exocyclic substituents such as phosphines, alkynes, arenes, cyclopentadienyl group etc., are considered for discussion in this section. Two types of phosphine ligands have been prepared and these are given in Figure 1.20 [74,75]. L6 in which a phosphino group is directly bound to the cyclophosphazene skeleton by a P - P bond reacts with $Cr(CO)_5(THF)$ or $Fe_2(CO)_9$ to afford the mononuclear complexes $L6.Cr(CO)_5$ or $L6.Fe(CO)_4$ [75]. L6 behaves as a monodentate ligand *via* the phosphino group. A triruthenium cluster $L6.Ru_3(CO)_{11}$ in which the phosphino group is bonded to a ruthenium atom is also obtained from the reaction of L6 with $Ru_3(CO)_{12}$. The ligating behaviour of L4 and L5 is complex in which the phosphino group is bonded with the cyclophosphazene through a spacer unit [74]. Thus with $[RhCl(CO)_2]_2$ and $Fe(CO)_3BZA$, L4 forms complexes of ligand-metal ratio 2 : 1, $(L4)_2$.M (M = RhCl(CO) and $Fe(CO)_3$) while with AuCl, $H_3Os_3(CO)_{10}$ and $Mn(CO)_2Cp(THF)$ it forms complexes of the type L4.M (M = AuCl, $H_2Os_3(CO)_{10}$ and $Mn(CO)_2Cp$). L5, a potential hexadentate ligand, coordinates in a monodentate or bidentate fashion towards a metal, leading to a series of polynuclear coordination compounds [74]. The osmium derivatives of L4 and L5 function as catalysts for the isomerization of 1-hexene to 2-hexene [74].

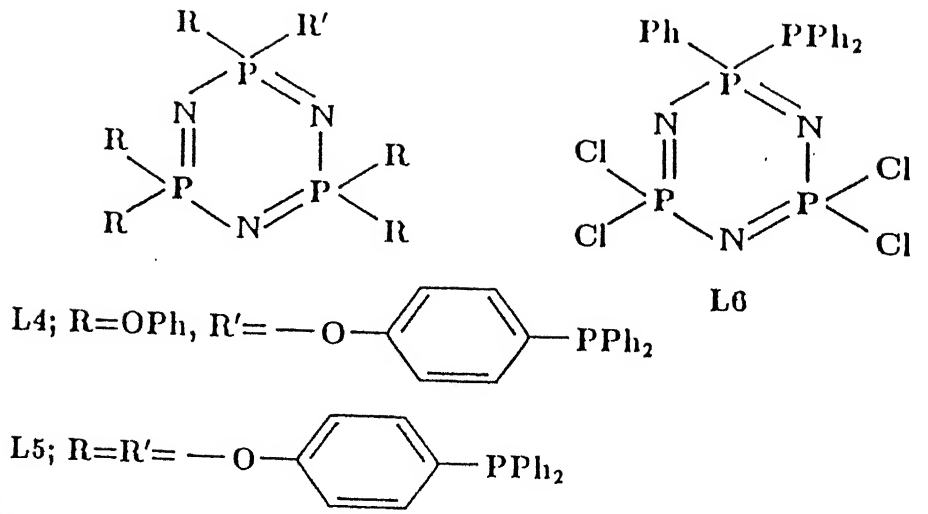
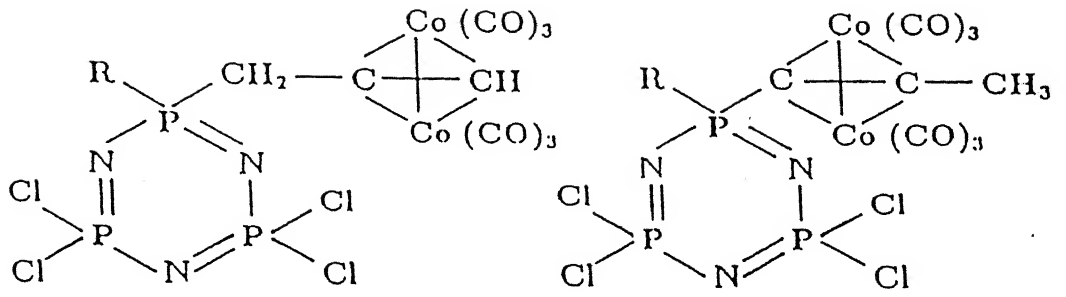


Figure 1.21: Structures of Cyclophosphazenes Containing Pendant Phosphino Groups.

A large number of alkynyl phosphazene bridging dicobalt complexes of the general formula $N_3P_3X_5C \equiv CR.Co_2(CO)_6$ have been synthesized starting from alkynyl phosphazenes, $N_3P_3X_5C \equiv CR$ ($R = SiMe_3, n-C_4H_9$, Ph and X= F) and $Co_2(CO)_8$ [76,77]. A novel tetracobalt cluster $2,2-N_3P_3F_4(C \equiv CPh.Co_2(CO)_6)_2$ has been obtained from the reaction of the alkynyl phosphazene, $2,2-N_3P_3F_4(C \equiv CPh)_2$ with $Co_2(CO)_8$ [76]. Allcock and coworkers have reported the formation of two series of π complexes from the alkynyl phosphazenes, with the general formula gem $N_3P_3Cl_4(R)(CH_2C \equiv CH).Co_2(CO)_6$ and $N_3P_3Cl_4(R)(C \equiv C-CH_3).Co_2(CO)_6$ where R = methyl, ethyl, n-propyl, isopropyl, n-butyl and allyl groups (Figure 1.22) [78]. In all these complexes only the alkynyl unit interacts with the cobalt carbonyl fragment and no interference is noticed from the skeletal nitrogen atoms (Figure 1.22). Interestingly some of these complexes are identified as promising cataysts for the cyclotrimerization of alkynes [78].



R=CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9 and C_3H_5(allyl)

Figure 1.22: Formation of π complexes from alkynyl phosphazenes.

Aryl phosphazenes form phosphazene (η^6-arene) $Cr(CO)_3$ complexes on treatment with $Cr(CO)_6$ [79]. Alternatively they are obtained by reacting the sodium salt of an alcoholic or phenolic chromium tricarbonyl complex with $N_3P_3Cl_6$. Figure 1.23 summarizes these reactions [79].

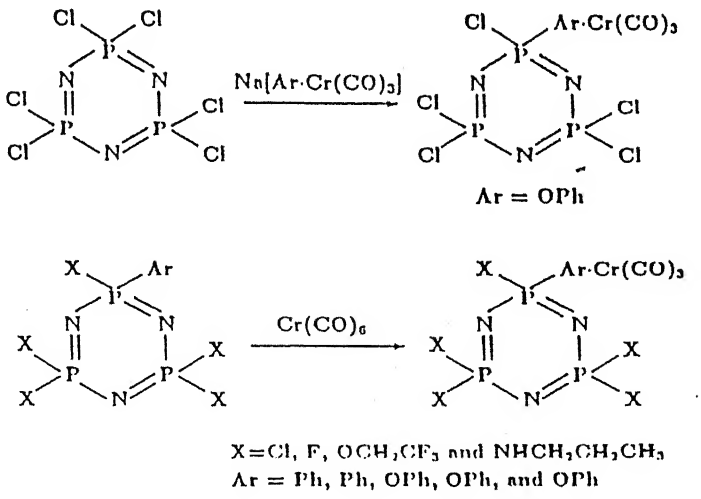


Figure 1.23: η^6- Complexes of Aryl Cyclotriphosphazenes.

Allcock and coworkers have prepared ferrocenyl or ruthenocenyl linked cyclophosphazenes by treating a lithioferrocene or ruthenocene with the halogenocyclophosphazenes [80-85]. Both the trimeric and tetrameric derivatives have been obtained. Depending on the mode of attachment of the metallocene to the cyclophosphazene ring they fall into two groups i.e., pendant (I) and transannular (II) linked derivatives (*cf.* Figure 1.24). Apart from this with cyclotetraphosphazenes an antipodally linked metallocene derivatives is also isolated [85]. Crystal structure of one such compound, $N_4P_4[(C_5H_4)_2Ru]_2$ is presented in Figure 1.25. Cyclic voltammetric studies of these compounds indicate that phosphazenes are highly electron withdrawing units, and give rise to a marked positive shift in the oxidation potentials compared to ferrocene [86]. Type II (*see* Figure 1.24) derivatives show shifts twice those of pendant analogs (Type I) suggesting the cumulative electron withdrawing effect of the phosphazene operating *via* each cyclopentadienyl ring. Also the crystal structure determinations reveal that in the trans annular linked complexes (Type II) the planarity of the cyclophosphazene ring is severely affected than that of Type I compounds [83-85].

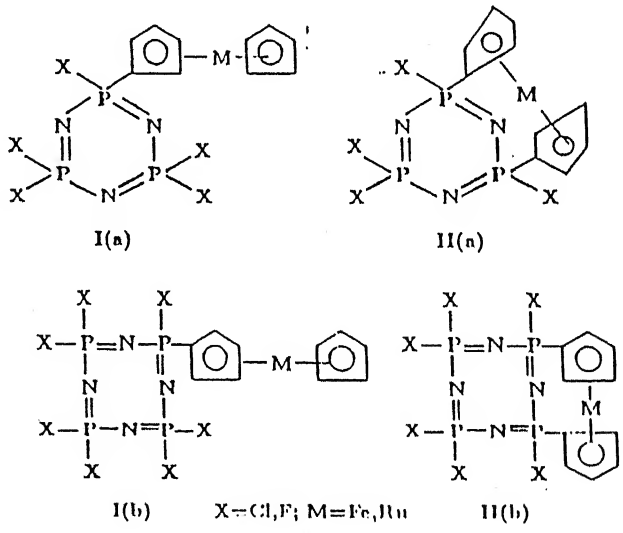


Figure 1.24: Types of Ferrocenyl Linked Cyclophosphazenes.

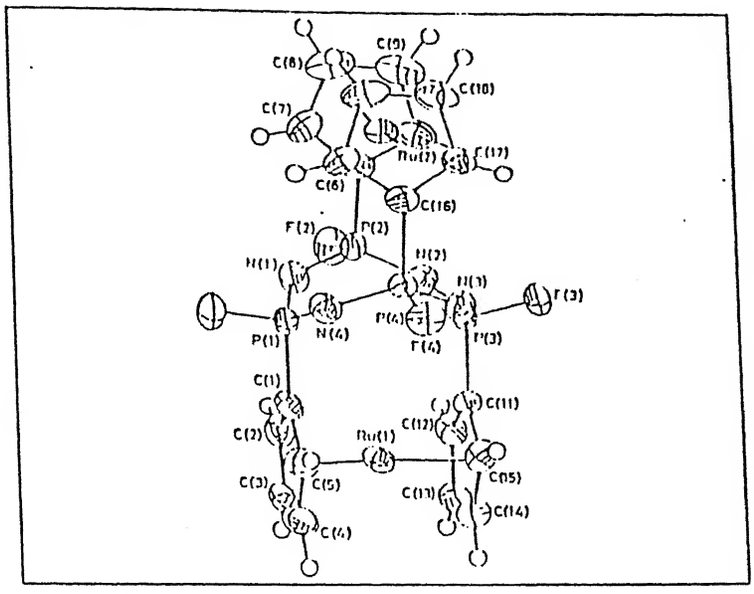


Figure 1.25: Crystal Structure of $N_4P_4[(C_5H_4)_2Ru]_2$.

1.3.6 Classical Donors

Cyclophosphazenes containing exocyclic substituents with classical donor sites such as nitrogen, sulfur etc., are very limited. In complex, $N_3P_3(NMe_2)_4[(NHCH_2CH_2NH)_2.NiCl_2]$ an exocyclic nitrogen participation in coordination is predicted from the spectroscopic evidence [87]. However, in complex $N_4P_4(NMe_2)_8.W(CO)_4$ (Figure 1.26) an endocyclic nitrogen is also coordinated to the metal as confirmed by crystal structure determination [88]. Cyclophosphazenes which bear six schiff base units as substituents form hexa nuclear complexes with zinc, palladium, and platinum halides [89]. Macro cycles such as porphyrin [90,91] and phthalocyanin [92] linked cyclophosphazenes have been synthesized and their metallation behaviour is found to be parallel to that of unsubstituted macrocycles. A pendant carboranyl group of a cyclophosphazene has been found to interact with metal carbonyls [93]. Thiol functionalized cyclotriphosphazene, $N_3P_3Ph_2(CH_3)(SH)(HL7)$ reacts with Ni, Pd and Pt chlorides to result in complexes M.$(L7)_2$ in which an exocyclic sulfur and an endocyclic nitrogen participate in coordination [94].

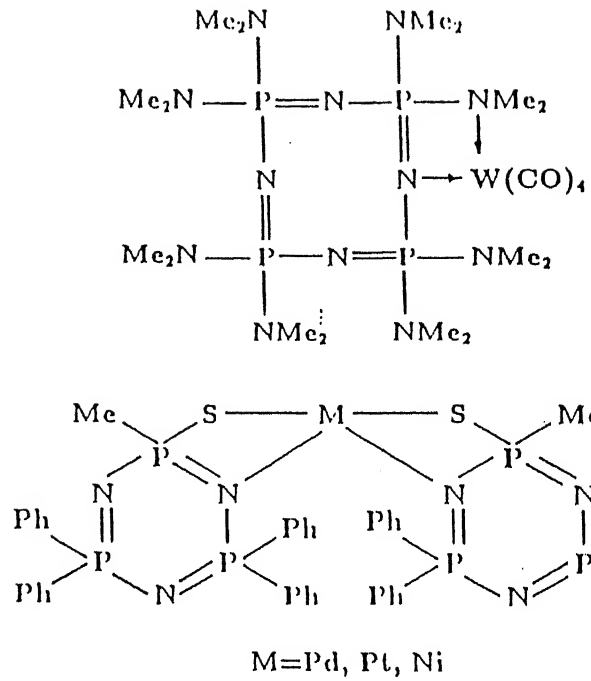


Figure 1.26: Examples of Exocyclic Group Participation in Coordination.

In addition to the above examples recently pyrazolyl cyclophosphazenes have been re investigated as suitable ligands for transition metal complexes [5-11]. $N_3P_3(Pz)_6$ (Pz = 3,5-dimethyl pyrazolyl) and $N_3P_3Ph_2(Pz)_4$ have been shown to interact in a novel N_3 nongeminal mode. Illustrative examples are shown in Figure 1.27. Also $N_3P_3(Pz)_6$ forms homo and hetero bimetallic derivatives [6].

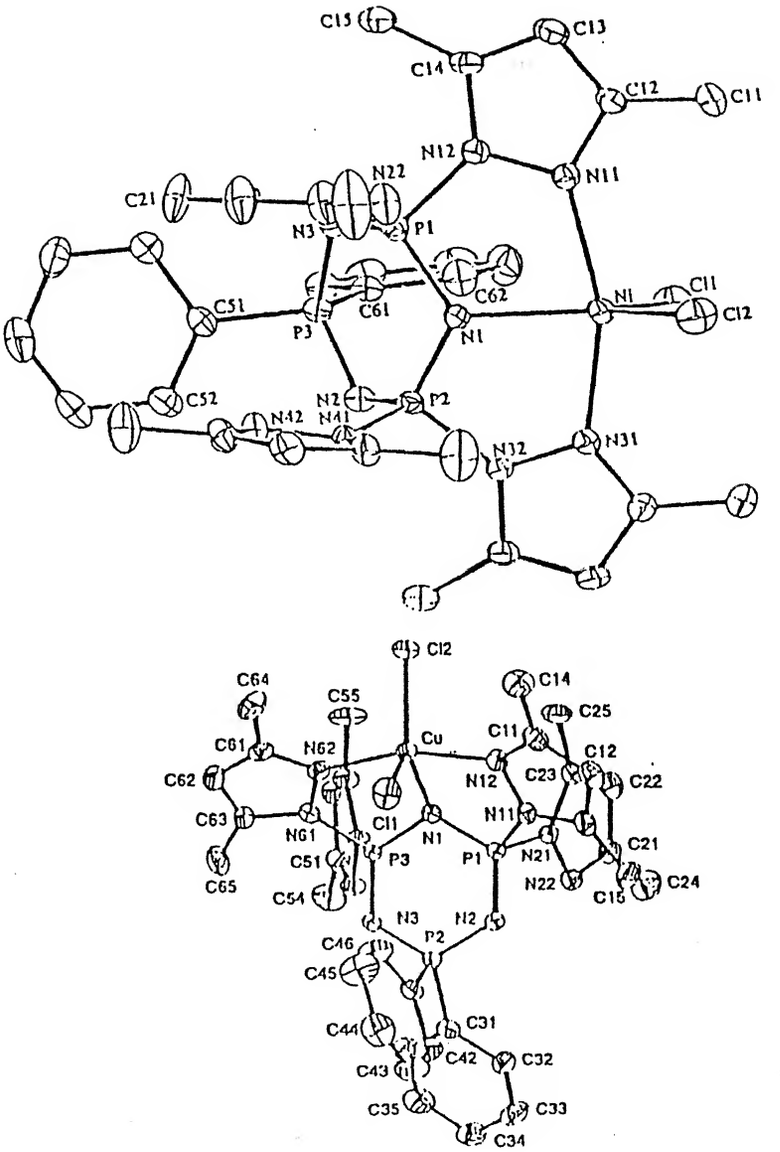


Figure 1.27: Examples of Pyrazolyl Phosphazenes Interacting *via* a Nongeminal Mode.

1.4 Polyphosphazenes

1.4.1 Synthesis of Polydichlorophosphazene by the Ring Opening Method

$N_3P_3Cl_6$ can be polymerized at 250°C in a vacuum sealed tube. However, at higher temperatures i.e., above the ceiling temperature of 350°C a depolymerization reaction has been found to occur giving rise to cyclic oligomers (Figure 1.28)[95-98].

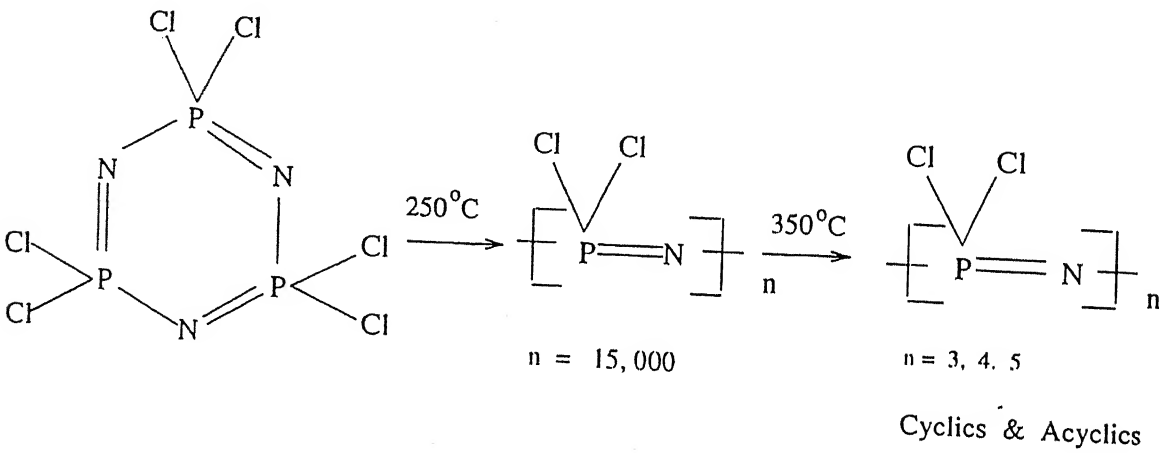


Figure 1.28: Polymerization and Depolymerization of $N_3P_3Cl_6$.

In the absence of any catalysts the above polymerization reaction is slow. However, several catalysts such as Lewis acids, metal hydrates or even traces of moisture have been found to be quite effective in accelarating the rate of polymerization [99-101]. The role of these catalysts is to presumably generate an initial phosphorus cation. This acts as an initiator for the further propagation of the polymerization. This mechanism is shown in Figure 1.29. However, increased amounts of water leads to crosslinking reactions leading to an insoluble gel like material. Table 1.1 summarizes the important catalysts used and their role in the yields of polymer obtained.

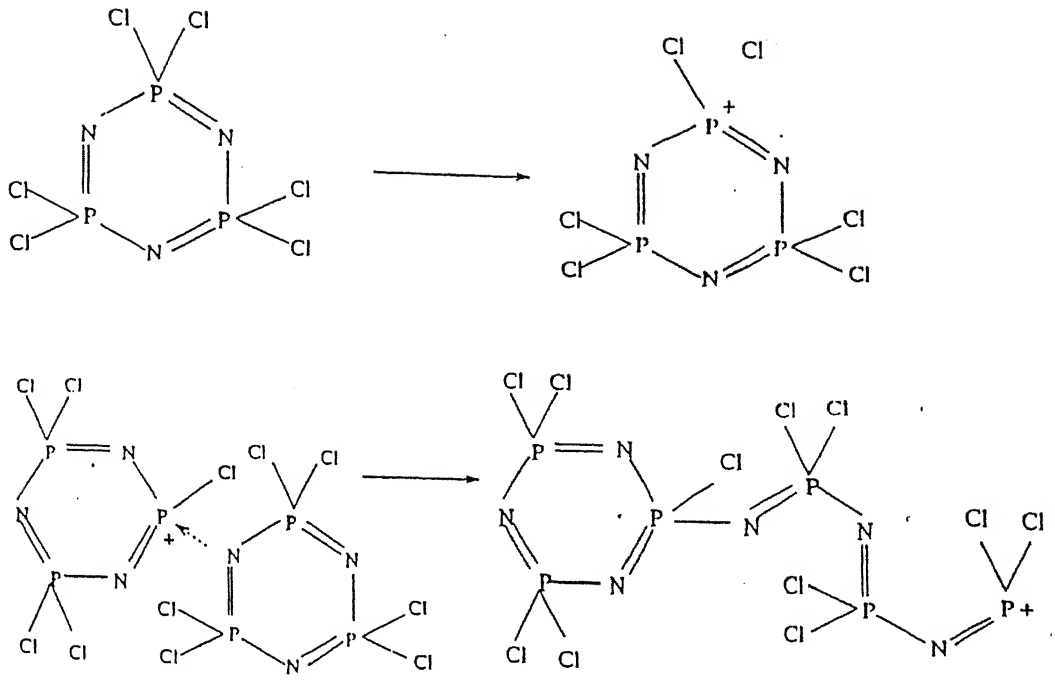


Figure 1.29: Mechanism for the Polymerization of $N_3P_3Cl_6$.

Table 1.1: Important Catalysts Used for the Polymerization of $N_3P_3Cl_6$.

Initiator	Amount mol%	Polymerization time (hrs)	Temperature °C	Soluble polymer %	Molecular weight Mw
PPh_3	3	12	250	27	5.3 x 10^6
$PhCO_2H$	7	4	250	64	5.8 x 10^4
$N_3P_3Cl_5(NPPh_3)$	3.8	120	250	68	2.3 x 10^5
$N_3P_3Cl_3(NMe_2)_3$	5	2.4	250	52	1.5 x 10^6
$CaSO_4.2H_2O$	17	14	250	66	5.1 x 10^6
$Sn(Ph)_4$	25	60	250	..	
BCl_3	0.66	48	210	95	6.0 x 10^6

It is clear that other mechanisms for polymerization must be present since some strained cyclophosphazenes lacking halogens do undergo polymerization; also permethyl cyclotriphosphazenes are known to undergo ring expansion[102](Figure 1.30).

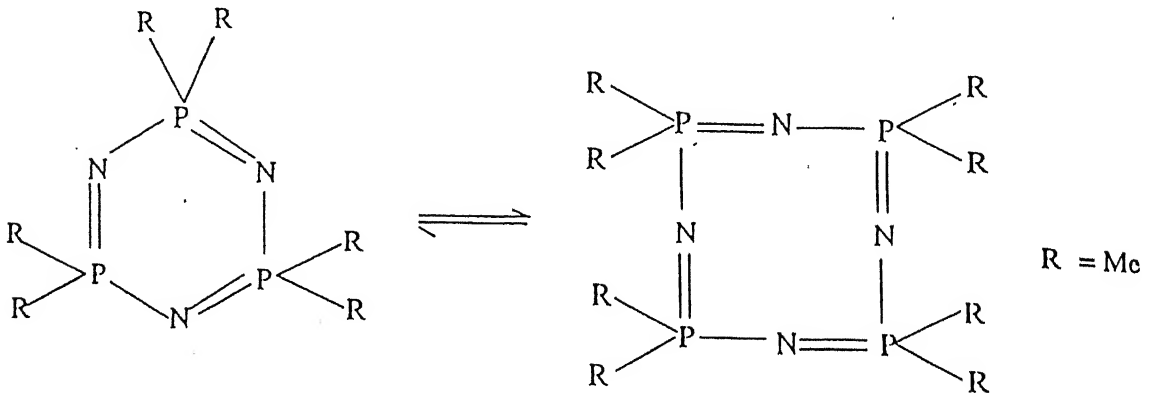


Figure 1.30: Example for Persubstituted Phosphazene Undergoing Ring Expansion.

Several other methods of preparing the polydichlorophosphazene are now known. These include solution polymerization, γ-irradiation polymerization, etc., [103-106]. However, the relative simplicity of the ring opening polymerization of $N_3P_3Cl_6$ has helped this method retain its prominence as a preparative route of choice.

In contrast to the polymerization of $N_3P_3Cl_6$ there are very few reports on the polymerization behaviour of other halogenocyclophosphazenes such as $N_3P_3F_6$ or $N_3P_3Br_6$. The fluoro polyphosphazene $(NPF_2)_n$ is a useful polymer since reactions of organometallic reagents with $(NPCl_2)_n$ afford only skeletal cleavage products while with the former skeletal cleavage does not occur till atleast 75% of the flourines are substituted. The skeletal cleavage is believed to proceed *via* the following mechanism (Figure 1.31).

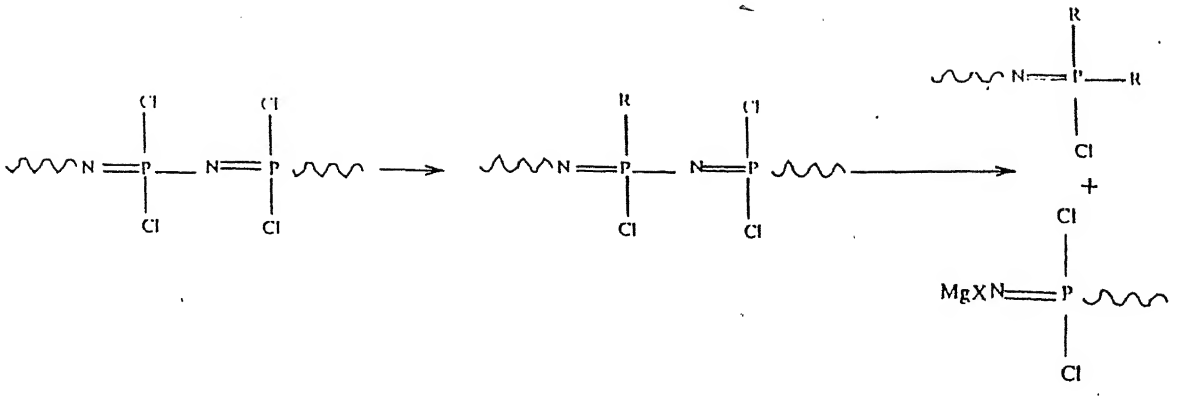


Figure 1.31: Mechanism of Skeletal Cleavage in Polyphosphazenes.

Although the fluoropolymer $(NPF_2)_n$ is interesting, unfortunately its insolubility in most organic solvents has precluded its usefulness.

1.4.2 Polyorganophosphazenes via the Macromolecular Substitution Route

As discussed *vide supra* polydichlorophosphazene is extremely reactive and sensitive to moisture. However, this feature of the polymer is also advantageous since P - Cl bonds can be substituted by a wide range of nucleophilic reagents affording polymers with varying structure and properties. Reactions with organometallic reagents usually lead to ring degraded products. Thus polyphosphazenes containing a P - C bond are not accessible from this synthetic route. They have to be prepared by an alternative procedure as will be discussed *vide infra*.

Using the macromolecular substitution route, more than 300 polymers have been

synthesized with varying properties. Thus a methyl amino substituted polymer $[NP(NH\ Me)_2]_n$ is water soluble and used as drug carrier, where as $[NP(CF_3CH_2O)_2]_n$ is a hydrophobic elastomer.

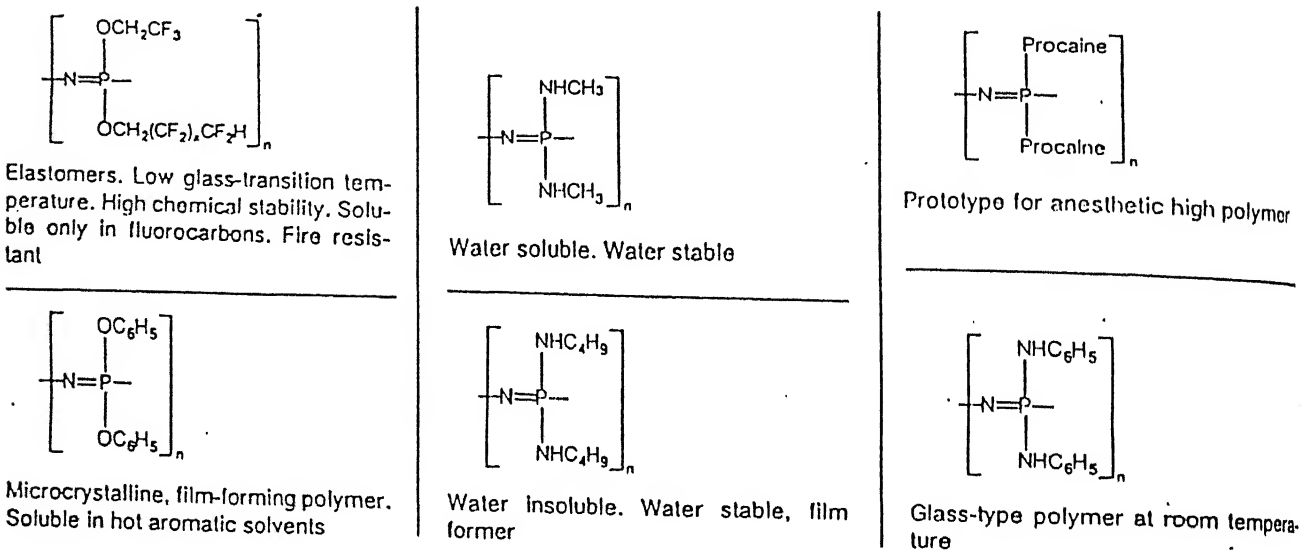


Figure 1.32: Structure Property Relationship Involved in Polyphosphazenes.

1.4.3 Condensation Polymerization Route for the Preparation of Polyalkyl and Polyarylcyclophosphazenes

Neilson and coworkers have developed a condensation polymerization method for the preparation of alkyl and aryl cyclophosphazenes [107]. The method as illustrated in Figure 1.33 consists of a multi step route. A mono phosphazene precursor containing a $NSiMe_3$ and a $P-OCH_2CF_3$ structural unit is the key synthon. Heating the precursor leads to the loss of $Me_3Si-OCH_2CF_3$ and in the formation of a high polymer containing P-alkyl or P-aryl substituents.

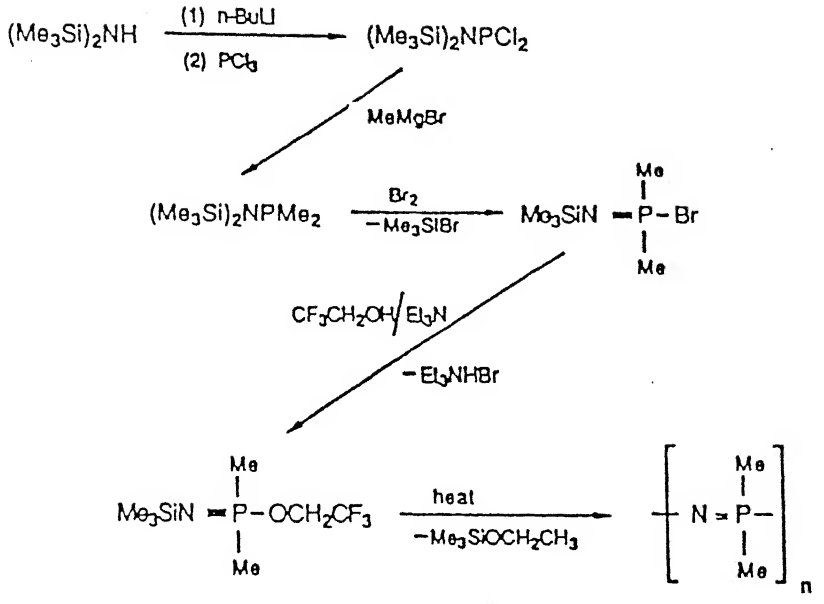


Figure 1.33: Synthetic Route for the Preparation of Alkyl and Aryl Phosphazene Polymers.

1.5 Pendant Cyclophosphazene containing Polymers

1.5.1 Homopolymerization of Cyclophosphazene Containing Organic Monomers.

The polymers discussed so far are inorganic backbone polymers with organic side groups on the phosphorus atom. In contrast to these kind of polymers, there has also been an interest to develop hybrid polymers containing an organic backbone and a cyclophosphazene ring as a pendant (side) group. The synthetic route to develop such a polymer is to introduce a polymerizable organic substituent on the phosphorus atom of the cyclophosphazene ring, and subsequently polymerizing such a derivative.

Allen and coworkers have synthesized cyclophosphazenes with exocyclic vinyl groups such as 2-(2-propenyl) pentafluorocyclotriphosphazene (1)[108], 2-(α- Ethoxyvinyl)

pentafluorocyclotriphosphazene (2)[109], and (α- methyl ethenyl)phenyl pentafluorocyclotriphosphazene (3)[110] (Figure 1.34). All of these have been synthesized by making use of the well developed substitution chemistry of halogenocyclophosphazenes. Since reactions of chlorocyclophosphazenes with alkyl or aryl lithium reagents leads to ring degraded products, fluorocyclophosphazene was the preferred starting material for the synthesis. However, Allen and coworkers have observed that these cyclophosphazene containing monomers (1), (2)and (3) could not be homopolymerized by free radical initiators at moderate temperatures. It was suggested by the authors that the σ- electron withdrawing effect of the cyclotriphosphazene ring depletes the electron density on the olefinic functionality and prevents the homopolymerization. However, these cyclotriphosphazenes could be copolymerized with certain organic monomers such as styrene or methyl methacrylate.

Inoue and coworkers have reported the synthesis and homopolymerization of [2-(4' -vinyl-4-biphenylyloxy)cyclotriphosphazene (CPHVB) [111]. Inoue and coworkers have also reported the flouro analogue (5)[111] and trifluoroethoxy derivatives (6) [111], 2-(p-metharyloxymethylphenoxy)pentakis(trifluoro ethoxy)cyclotriphosphazene (7) [112], and 2-(4-methacryloxyphenoxy)penta chlorophosphazene (8)[113], which also undergo homopolymerization. In an extension of their earlier work, Inoue and coworkers have recently reported the polymerization studies on the styrene derivatives containing multi armed oligooxy ethylene cyclotriphosphazenes. These polymers have been shown to function as polymer solid electrolytes when complexed with lithium salts in the solid state [114].

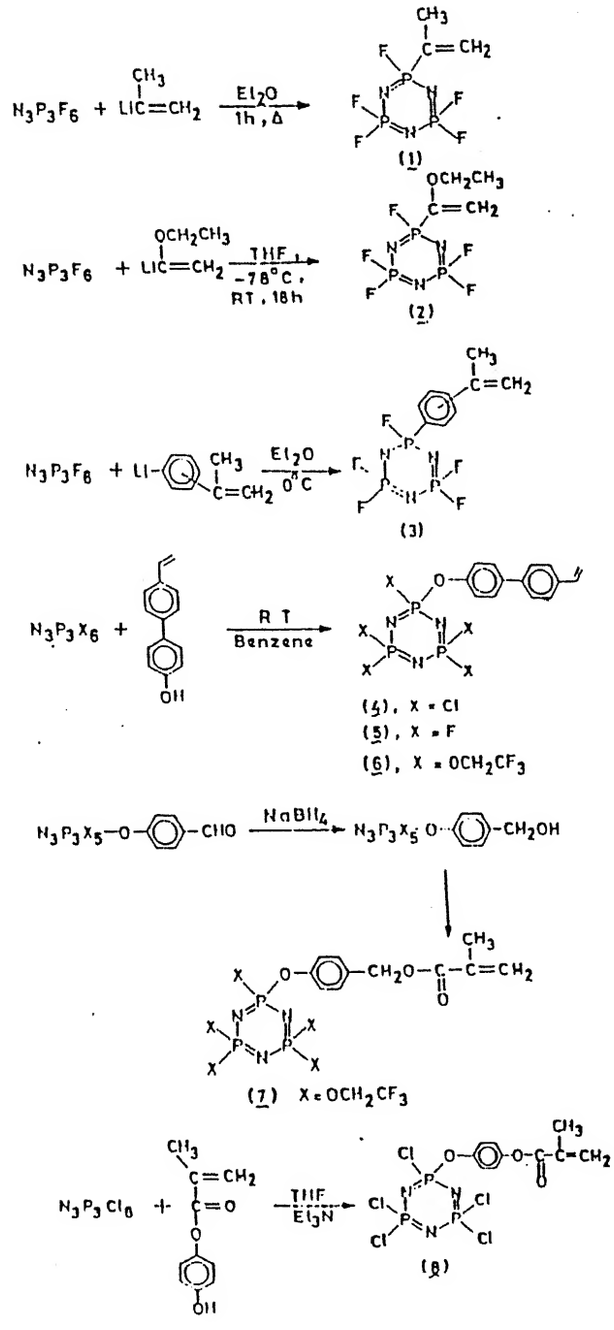


Figure 1.34: Examples of Phosphazene Pendant Monomers.

Recently Selvaraj and coworkers have described the copolymerization studies of $N_3P_3Cl_5(C_{14}H_{11}O)$ (CPHVB) and have found that it readily forms copolymers with methyl acrylate, ethyl acrylate, methyl methacrylate and styrene. All the copolymers were found to be highly thermally stable [115].

1.6 Structure of Polyphosphazenes

1.6.1 General Features

NMR spectroscopy is a valuable tool in the identification of polyphosphazenes. Thus $[NPCl_2]_n$ is highly shielded and the phosphorus resonance for this polymer is seen at - 20.0 ppm in contrast to the cyclic $N_3P_3Cl_6$ where the chemical shift is seen at + 19.5 ppm [16]. Spectral changes occur as the chlorines are substituted in the polymer by other substituents. Table 1.2 gives ^{31}P NMR values for some selected polymers.

The macromolecular conformation of polyphosphazenes is different from other macromolecules since in the former the side groups are attached to every *other* skeleton atom rather than to every skeleton atom in chain as found in the latter. Secondly the bonding in these polymers is not a classical $p_\pi - p_\pi$ type and therefore does not impose torsional barriers. Of the two extreme limits the polymer conformation as defined by the torsional angles assumed by the backbone bonds, the cis-trans planar conformation which allows the side groups to be as far away from each other as possible, is adopted by polyphosphazenes (Figure 1.35). This is supported by molecular mechanics calculation and by X-Ray diffraction studies [116,117].

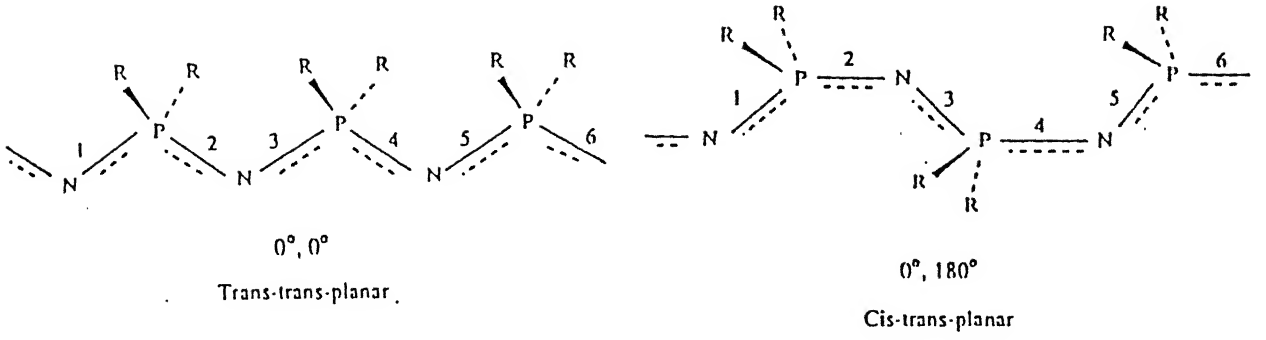


Figure 1.35: Conformations of Polyphosphazene.

1.6.2 Bonding and Skeletal Flexibility

As discussed for cyclophosphazenes, each phosphorus and nitrogen have five valence electrons each. Of these the phosphorus forms its σ bonds with four electrons and the nitrogen with two. This leaves a lone pair and a lone electron on nitrogen and a lone electron on phosphorus. The nitrogen lone electron present in a $2p_z$ orbital and the lone electron of phosphorus present in a 3d orbital can give rise to a π bonding scheme as shown below (Figure 1.36).

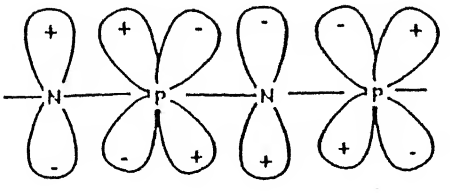


Figure 1.36: Π Bonding Scheme for Polyphosphazene.

Because each phosphorus atom can use as many as five 3d orbitals, torsion of a P-N bond can bring the nitrogen p-orbital in to an overlapping position with a d orbital at virtually any torsion angle. Thus the torsional barriers are very small in the backbone bonds and may be as low as 0.1 Kcal per bond ! This is reflected in th low T_g's exhibited by these polymers. Thus $[NPCl_2]_n$ has a T_g of - 66°C, $[NPF_2]_n$(- 96°C), $[NP(OCH_3)_2]_n$ (- 74°C) etc., However, large inflexible side groups that generate their own steric restrictions independent of backbone torsional barrier lead to higher T_g's as seen for $[NP(OPh)_2]_n$ (-8° C) or $[NP(OC_6H_9Ph-p)_2]_n$ (+ 91°C) or $[NP(NHPh)_2]_n$ (+ 91°C). Some of the T_g's of various types of these polymers is listed in Table 1.2.

Table 1.2: Physical Properties of Selected Polyphosphazenes.

Polymers	$^{31}PNMR$	$T_g^\circ C$	M_w
$[NP(Me)_2]_n$	8.3	-46	1x 10^6
$[NP(OPh)_2]_n$	-18.3	-9	3x10^6
$[NP(OMe)_2]_n$	-3.5	-76	6 x 10^6
$[NP(OCH_2CF_3)_2]_n$	-7.2	-66	1 x 10^6
$[NP(NHC_3H_7)_2]_n$	-3.9	4	1 x 10^6
$[NP(NHPh)_2]_n$	-	9.1	1 x 10^6

Some of the structure property relationships are also shown in Table 1.3. Thus side groups such as $NHCH_3$, $OCH_2CH_2OCH_2CH_2OCH_3$, glucosyl, glyceryl etc., generate solubility in water. Groups such as OCH_2CF_3 or OPh render the polymer hydrophobic. Microcrystalline polymers are obtained when the side groups are F, Cl, CH_3, OCH_2CF_3, OC_6H_5 etc., where as most amino phosphazene polymers are amorphous.

Table 1.3. Structure Property Relationship of Selected Polyphosphazenes.

Compounds	Properties
$[NPCl_2]_n$	Elastomer, hydrolytically unstable.
$[NPF_2]_n$	Elastomer, hydrolytically unstable.
$[NPBr_2]_n$	Leathery material: Hydrolytically unstable.
$[NP(OMe)_2]_n$	Elastomer .
$[NP(NHMe)_2]_n$	Glass : Water soluble.
$[NP(OPh)_2]_n$	Microcrystalline, thermoplastic.
$[NP(OCH_2CF_3)_2]_n$	Microcrystalline and thermoplastic.
$[NP(ONHPh)_2]_n$	Glass.

1.7 Research Problem Undertaken in This Thesis

This thesis explores the design of new polyphosphazenes containing organic side groups as well as pendant cyclophosphazene containing organic polymers. Also work on pyrazolyl substituted cyclo and polyphosphazenes suitable for interaction with transition metals has been carried out.

Although several polyphosphazenes with varying substituents are known the number of primary amino substituted derivatives are still quite limited and almost no examples of cyclic amino containing polyphosphazenes are known in literature. *Chapter II* describes the polyphosphazenes containing three cyclic amines, cyclopropylamine, cyclopentylamine, and cyclohexylamine. Model compound studies have been carried out on the six membered $N_3P_3Cl_6$ as well as eight membered $N_4P_4Cl_8$. X-Ray structures of two derivatives are reported, *viz.*, gem $N_3P_3Cl_2(NHC_6H_{11})_4$ and $N_4P_4(NHC_3H_5)_8$.

As discussed earlier there are relatively few examples of cyclotriphosphazene pendant organic polymers and none containing cyclotetraphosphazene as a pendant group.

In *Chapter III* a discussion on the synthetic strategies for the preparation of three new cyclotetraphosphazene containing organic monomers is investigated. Attempts to homopolymerize these new types of cyclophosphazene reagents have also been discussed.

Chapter IV describes phosphazene polymers capable of interaction with transition metals. Two types of systems have been designed. X-Ray structures of small molecules $N_3P_3(Pz)_6$, $N_3P_3(NH_2)_2(Pz)_4$. $CoCl_2$, $N_4P_4(Pz)_4$ $(OH)_2.CuCl_2$ and $(Pz)_2.CoCl_2$ are also described.

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Chapter 2

Cyclic Amino Substituted Cyclo and Polyphosphazenes

2.1 Introduction

The reactions of $N_3P_3Cl_6$ and $N_4P_4Cl_8$ with amines have been well studied [1 – 5]. The chlorine replacement reactions with amines (or other nucleophilic reagents) can proceed to afford several kinds of products with varying regio and stereo dispositions. These possibilities have been discussed in chapter one. (*see* Figures 1.2 and 1.3 in Chapter one.)

Thus the reactions of $N_3P_3Cl_6$ with nucleophilic reagents can afford three different products at the bis, tris and tetrakis stages. In contrast the reactions with $N_4P_4Cl_8$ can give rise to even more complex possibilities. The mechanistic aspect on the reactions of amines with $N_3P_3Cl_6$ reveals that where as secondary amines such as dimethyl amine preferentially react to afford nongeminal products [6-8], the situation with primary amines is more complex. Sterically hindered amines such as t-butyl amine affords geminally substituted products [9] where as with amines such as ethyl amine, substitution occurs *via* a nongeminal route [10,11] (*see* Figure 2.1).

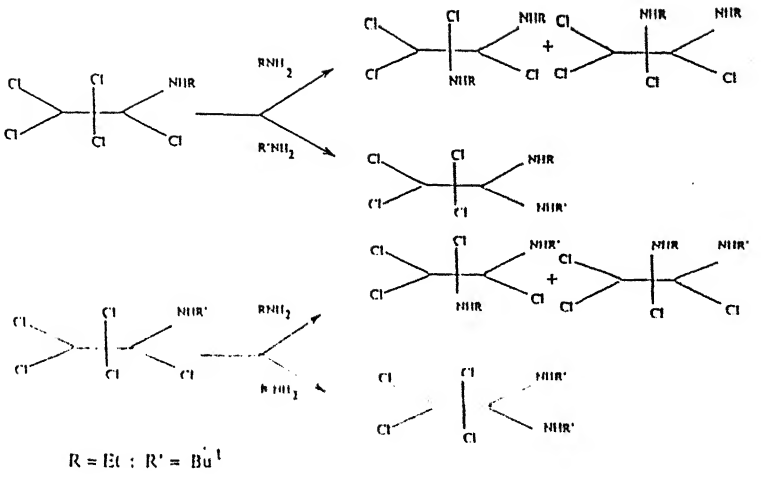

Figure 2.1: Substitution Pattern in Mixed Amino Derivatives.

Table 2.1 summarizes some of the product pattern obtained in the reaction of $N_3P_3Cl_6$ with various amines.

Table 2.1: Reactions $N_3P_3Cl_6$ with Various Amines

No.	Amine HNRR'		Products $N_3P_3(NRR')_nCl_{6-n}$			Ref.
	R	R'	n = 2	n = 3	n = 4	
1[c]	H	H	g	ni	ni	12
2[d]	H	Me	ng(t > c) > g	ni	ni	13, 14
3	H	Et	ng(t)	ng(tr)	g(tr)	10,11
4	H	CH_2CH_2Cl	g	tr(u)	g	15
5	H	CH_2CH_2OMe	ng	tr(u)	g	15
6	H	CH_2CH_2COOEt	g	ni	g	16
7	H	CH_2Ph	ng(t) > g	ni	g	17
8	H	Pr^i	ng(t > c) > g	ni	g	10,11
9[e]	H	Ph	g, ng	s	g	18,19
10[e,f]	H	$C_6H_4OCH_3$-*p*	ng(c = t), g	g = ng(c = t)	g	19
11	H	Bu^t	g	ni	g	9
12	Me	Me	ng(t > c) > g	ng(t > c) = g	ng(c)	6-8
13	Et	Et	ng(t > c)	ng(t > c) > g	ng(t > c)	20
14[f]	NC_2H_4		g > ng(c < t)	g > ng(c < t)	g > ng(c = t)	21,22
15	NC_5H_{10}		ng(t > c)	ng(t) > g	ng(c)	23
16	Me	Ph	ng(c = t)	ng(c) = g	ni	24
17[d]	CH_2Ph	CH_2Ph	ng(u)	ni	ni	17
18[d]	N=PPh$_3$		ng(u)	ni	ni	13b

[a] g = geminal, ng = nongeminal, t = *trans*, c = *cis*, tr = trace amount isolated, ni = not isolated or identified, s = spectroscopically identified in mixture but not isolated, u = isomers isolated, configuration unassigned.

[b] In most cases mono and persubstituted derivatives were isolated and pentakis derivatives remained elusive.

[c] mono derivative has been obtained indirectly by treating the geminal bis derivative with HCl in refluxing toluene.

[d] hexakis derivative was not isolated

[e] At the bis stage geminal product was obtained in THF with Et_3N as HCl scavenger.

[f] pentakis derivative $N_3P_3Cl(NRR')_5$ isolated.

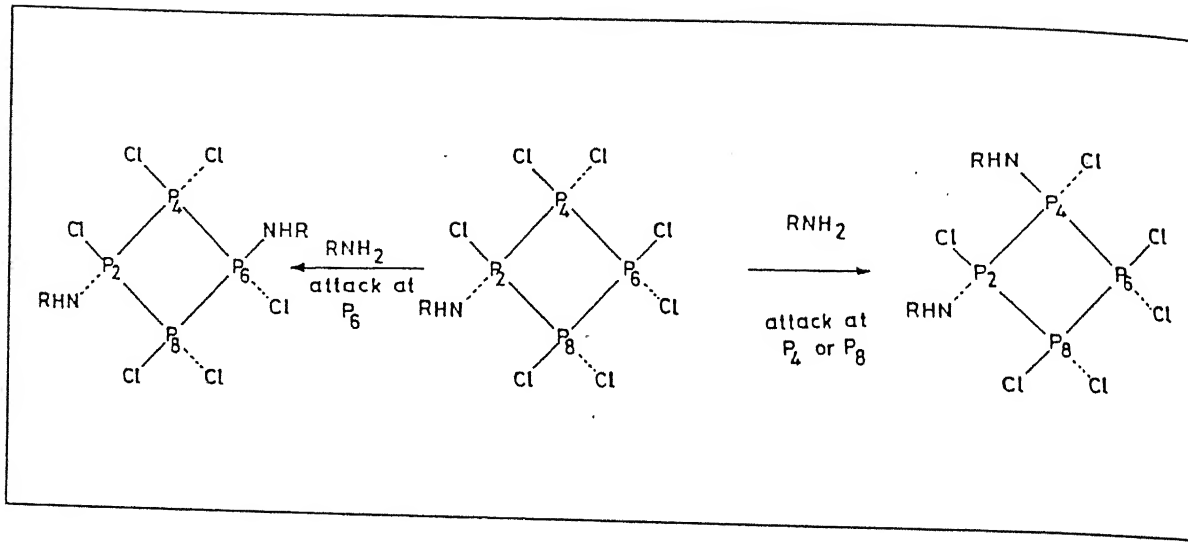

Figure 2.2: Formation of 2,4 and 2,6 Derivatives with $N_4P_4Cl_8$.

In contrast to the situation observed with $N_3P_3Cl_6$, the nucleophilic substitution reactions of amines with $N_4P_4Cl_8$ *always* proceed in a nongeminal manner. Also the nucleophilic substitution reactions of $N_4P_4Cl_8$ are much faster than the corresponding reactions with $N_3P_3Cl_6$ [25-31]. This enhanced reactivity is as a result of the flexibility of the cyclotetraphosphazene which is generally found in puckered conformation in contrast to the planar conformation observed in six membered rings. It is believed that nucleophilic substitution reactions which can proceed *via* an S_N2 path way require the formation of a penta coordinate transition state at phosphorus. Such a transition state is easily achieved by the more flexible eight membered ring rather than the planar six membered systems. Also, the presence of an amino substituent increases the electron density at phosphorus and depletes its nucleophilicity. It is therefore believed that the incoming nucleophile prefers attack at a nongeminal centre. Additionally at the bis stage the possible regio selectivity is between the 2, 4 and 2, 6 substituted products (*see* Figure 2.2). Table 2.2 summarizes the reactions of various amines with $N_4P_4Cl_8$.

Table 2.2: Reactions of Amines HNRR' with $N_4P_4Cl_8$[a].

No	Amine HNRR'		Products $N_4P_4Cl_{8-n}(NRR')_n$			
	R	R'	n = 2	n = 3	n = 4	n = 5
1[b]	H	Et	2, t-6	2, c-4, t-6	2, c-4, t-6, t-8 2, c-4, c-6, t-8	ni
2	H	Bu^t	2, 6 & 2, 4(u)	2, 4, 6(u)	ni	ni
3[d]	Me	Me	2, t-6	2, c-4, t-6 2, t-4, t-6 2, 2, 6	2, t-4, t-6, t-8 2, c-4, t-6, c-8 2, c-4, t-6, t-8 2, 2, 6, 6	2, 2, 4, t-6, t-8 2, 2, 4, 6, 6
4[d,e]	Me	Ph	2, t-6 2, t-4	2, c-4, c-6 2, t-4, t-6	2, c-4, t-6, t-8 2, 2, 6, 6 2, c-4, c-6, t-8 2, t-4, t-6, t-8 2, 2, 4, t-6	ni
5[c,b]	CH_2Ph	CH_2Ph	2, t-6 2, t-4	ng(u)	ng(u)	ni
6[e]	NC_2H_4		2, 2 < 2, 4 (c > t) < 2, 6 (t > c)	2, 2, 6 2, t-4, c-6 2, c-4, t-6 2, 2, 4[f] 2, c-4, c-6[f]	ni	ni

[a] In most cases mono and octakis derivatives are isolated. In all reactions heptakis derivative remained elusive. Legend: c = *cis*, t = *trans*, ni = not isolated, u = isomers obtained but structures unassigned.
[b] Bicyclic derivative of formula $N_4P_4(NRR')_6(NR')$ isolated.
[d] Hexakis derivative of configuration 2, 2, 4, *t*-8, 6, 6 isolated.
[e] Octakis derivative not isolated.

The reactions of difunctional reagents with halogenocyclotriphosphazene have also been studied [32-36] and it is now known that the reaction can afford atleast four products (*see* Figure 2.3). Spirocyclic product is formed as a result of replacement of both chlorines on the same phosphorus atom, while the ansa product is formed as a result of the replacement of chlorines from two distinct phosphorus atoms with in the same molecule. In the open chain product only one end of the difunctional reagent is involved in the reaction with the chlorocyclophosphazene. Finally, intermolecular bridged products result from the reaction of two chlorocyclophosphazene molecules

with a difunctional reagent. This last reaction also is a model reaction for condensation polymerization involving phosphazenes. However, the spirocyclic reaction pathway is the most predominant one [37]. Ansa products have been rare [38-46]. More recently Shreeve and coworkers have also studied reactions of fluoro analogs [47,48].

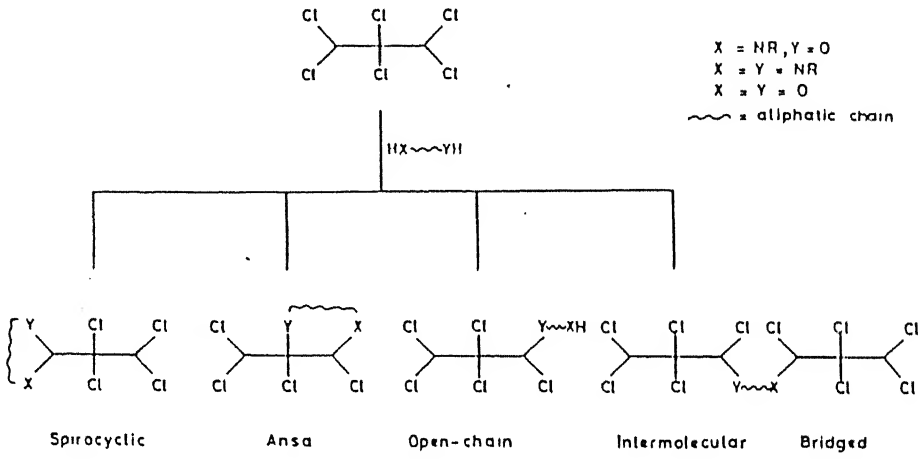

Figure 2.3: Reactions of $N_3P_3Cl_6$ with Difunctional Reagents.

Although several phosphazenes are known with varying types of substituents it is interesting to note that only a few primary amino substituted polyphosphazenes have been reported [49,50]. This paucity is likely because of the primary amino group functioning as crosslinking agent and serving to cross link different chains [50] (*see* Figure 2.4). The crosslinking mechanism in primary amines is largely controlled by steric factors [49,50]. It was found that cross linking readily occurs when polydichlorophosphazene reacts with ammonia, but shows little tendency for crosslinking when methylamine was employed. In the case of ethylamine, n-propylamine and n-butylamine no crosslinked products were observed. The alkyl chain attached to the amino function prevents the lone pair of electrons on the nitrogen from attacking the phosphorus centre of the near by chain. When the amino substituents are sterically encumbered, only partial replacement of chlorines is observed as found with amines such as isopropyl amine and other branched amines [50].

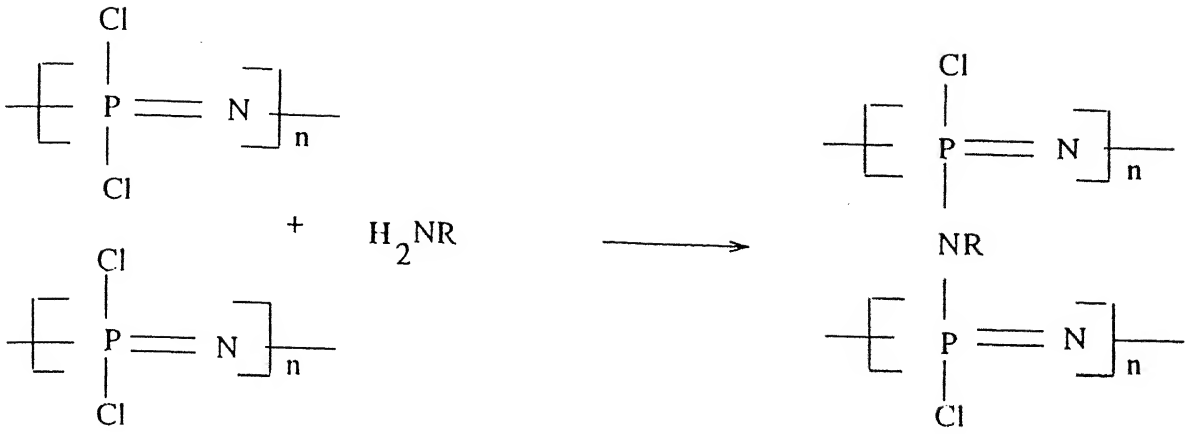

Figure 2.4: Crosslinking in Polyphosphazenes.

In order to explore the synthesis of cyclic amino polyphosphazenes, no examples of which are known in literature, we have chosen to study the reactions of polydichlorophosphazenes $[NPCl_2]_n$ with cyclopropylamine, cyclopentylamine and cyclohexylamine. It was interesting to ~~find out~~ learn if in these reactions normal substitution competes with crosslinking. Secondly the polymers obtained could be compared with straight chain amino substituted polyphosphazenes. We ~~have~~ chosen to study the reactions of these amines with $N_3P_3Cl_6$ and $N_4P_4Cl_8$. We reasoned that $N_4P_4Cl_8$ is structurally closer to the polymer, being flexible, and more reactive. Also the ^{31}P NMR chemical shifts of the eight membered ring are upfield to that of the analogous six membered systems a feature which is shared by the linear polymeric system also. During the course of this study we have successfully assembled nearly fully substituted polyphosphazenes poly[bis(cyclohexylamino)phosphazene] (CAPCP), poly[bis(cyclopentylamino)phosphazene] (CAPEP), and poly[bis(cyclopropylamino) phosphazene] (CAPRP). ~~Studies on~~ Reactions with the cyclic compounds afforded only partially substituted derivatives with $N_3P_3Cl_6$ where as under the same conditions fully substituted derivatives were accessible from $N_4P_4Cl_8$. We also undertook x-ray crystal structure studies of 2,2-dichloro-4,4,6,6-tetrakis(cyclohexylamino)cyclotriphosphazene (DCHEA) and 2,2,4,4,6,6,8,8-octakis(cyclopropylamino)cyclotetraphosphazene (OCPRA). The following account gives details of our investigations.

2.2 Experimental

2.2.1 Materials

Hexachlorotriphosphazene($N_3P_3Cl_6$) and octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) (Nippon soda, Japan) were recrystallized from petroleum ether (60°C - 80°C) and n-pentane respectively to constant melting (114°C, 123°C) solids before use. Cyclopropylamine, cyclopentylamine and cyclohexylamine (Fluka, Switzerland) were used as received. Triethyl amine was distilled over potassium hydroxide pellets prior to use. All organic solvents were dried and distilled by conventional methods [51]. Polydichlorophosphazene was synthesized by melt polymerization of hexachlorocyclotriphosphazene [52].

2.2.2 Analysis and Measurements

Infrared spectra were obtained as pressed KBr pellets on a Perkin-Elmer FT-IR 1600 spectrophotometer. NMR spectra in $CDCl_3$ were recorded on a Bruker WM 400 spectrometer operating at 400 MHz (^1H), and 135 MHz (^{31}P) respectively. Tetramethylsilane (^1H) was used as an internal standard, while 85% phosphoric acid (^{31}P) was employed as an external reference. Mass spectra were recorded on a JEOL Sx 102/DA 6000 mass spectrometer using xenon (6Kv, 10mA) as the FAB gas. The accelerating voltage was 10 Kv and the spectra were recorded at room temperature. C, H and N analyses were performed at the micro analytical centre, Central Drug Research Institute, Lucknow. X- ray powder diffraction studies were carried out on a Rich-Seifort(Iso debye flex 200 2D) instrument using Cu K_α radition operating at 30 Kv. Structure determination for small molecule cyclophosphazene model compounds were carried out on a Enraf-Nonius CAD-4 diffractometer with a monochromatic Mo K_α radiation. Solution grown crystals were glued on a glass fiber with silicon glue and mounted on the diffractometer. NRC 386 (PC version of NRCVAX) program was used to determine

the structure. Data collection was done at 293 K using θ -2 θ scan technique.

2.2.3 Measurement of Dilute Solution Viscosity [53]

The viscosity of the dilute polymer solutions can be related to the molecular weight of the polymer by Mark-Houwink equation.

$$[\eta] = KM^a$$

where 'K' and 'a' are constants. The intrinsic viscosity can be obtained by plotting the reduced viscosity of a series of polymer solutions of various concentrations against the solution concentration. Extrapolation to zero concentration yields the intrinsic viscosity. The intrinsic viscosity was determined experimentally by measuring flow times of the solvent (t_0) for a series of dilute polymer solutions of known concentration (t_c)in a SCHOTT GERÄTE ubbholde viscometer at 30°C using tetrahydrofuran as a solvent.

The intrinsic viscosity can be calculated by plotting $\eta_{Sp/C}$ versus concentration and exrapolation to zero concentration. The unit of intrinsic viscosity is expressed in cc/g. Differential thermal analysis (DTA) and differential scanning calorimetry were done on a SHIMADZU DTA - 50, General V4.1C DUPONT 2000 thermal analysers at a heating rate of 5°C per minute.Thermal gravimetric analysis (TGA) was carried out on a TGA V5.1A DUPONT 2100 thermal analyzer in nitrogen atmosphere at a heating rate of 50°C per minute.

2.3 Synthesis of 2,2-dichloro-4,4,6,6-tetrakis-(cyclicamino)derivatives

2.3.1 Synthesis of 2,2-dichloro-4,4,6,6-tetrakis(cyclohexylamino)-cyclotriphosphazene (DCHEA)

To a stirred solution of hexachlorocyclotriphosphazene (5.0g, 0.01mol) in benzene, a mixture of cyclohexylamine (8.5g, 0.09mol) and triethylamine (8.7g, 0.09mol) in benzene was added dropwise. The mixture was stirred at room temperature for 12 hours and then refluxed at 80°C for another 12 hours. Amine hydrochloride was separated by filtration. The solvent was evaporated under reduced pressure to get an oily liquid. The oily liquid was subjected to silica gel column chromatography. Initial elution with hexane resulted in the separation of unreacted $N_3P_3Cl_6$. DCHEA comes out with 50% ethyl acetate and 50% hexane mixture as the eluent (3.5g, 41%).

Melting point : 158°C.

Infrared (cm^{-1}) : 3320(w), 2940(s), 2860(s), 1440(s), 1410(s),1210(m),1160(m), 1100(m),900(s),730(s).

^{1} H NMR (δ) : 1.5 (m, 44H, CH_3,CH) ;3.0 (br.Singlet, 4H, NH).

^{31} P NMR (δ) : 22.6 (t, 1P, PCl_2), 20.9 (d, 2P, $P(NHR)_2$), $^2J_{P-P}$ = 49.4 Hz.

FAB Mass ($C_{24}H_{48}N_7P_3Cl_2$) : 598 ; found (M^+) = 598.

2.3.2 Synthesis of 2,2-dichloro-4,4,6,6-tetrakis(cyclopentylamino) cyclotriphosphazene (DCPEA)

Hexachlorocyclotriphosphazene (5.0g, 0.01mol) in 150 ml benzene was taken in a 250 ml round-bottomed flask. To this a mixture of cyclopentylamine (7.4g, 0.09mol) and triethyl amine (8.7g, 0.09mol) was added slowly. The mixture was stirred at room

temperature for 12 hours and then at reflux condition (80° C) for another 12 hours. The mixture was brought to room temperature. Precipitated amine hydrochloride salts were separated by filtration. The solvent benzene was stripped off in vacuum to get an oily liquid. Silica gel slurry was made from the oily mixture. Unreacted pure $N_3P_3Cl_6$ was recovered in the first fraction when eluted with benzene, DCPEA comes out with 25% ethylacetate / 75% benzene mixture as the eluent (3.9g, 50%).

Melting point : 144°C.

Infrared (cm^{-1}) : 3220(w), 2960(s), 1450(vs), 1210(s), 1160 (m), 1100(s) 810(m).

^{1}H NMR (δ) :1.8 (m, 36H, CH_3,CH), 3.6 (br.Singlet, 4H, NH).

^{31}P NMR (δ) : 23.0 (t, 1P, PCl_2), 10.3 (d, 2P, $P(NHR)_2$), $^2J_{P-P}$ = 48.2 Hz.

FAB Mass ($C_{20}H_{40}N_3P_3Cl_2$) : 542, found (M^+) = 542.

2.3.3 Synthesis of 2,2-dichloro-4,4,6,6-tetrakis(cyclopropylamino) cyclotriphosphazene (DCPRA)

Hexachlorocyclotriphosphazene (5.0g, 0.01mol) was taken in a 250ml round-bottomed flask. To this a mixture of cyclopropylamine (4.9g, 0.09mol) and triethylamine (8.7g, 0.09mol) was added dropwise. The reaction mixture turns turbid after the addition of amines, indicating the formation of amine hydrochloride. The reaction mixture was stirred at room temperature for 12 hours and then at boiling condition (80°C) for another 12 hours. The mixture was brought to room temperature. Amine hydrochloride was separated by filtration. The solvent was evaporated under reduced pressure to get an oily liquid. The oily liquid was subjected to silica gel column chromatography. Eluting with benzene gave unreacted $N_3P_3Cl_6$. DCPRA was obtained (3.9g, 62%) with 25% ethyl acetate / 75% benzene mixtures as the eluent.

Melting point : 138°C.

Infrared (cm^{-1}) : 3240(w), 3000(s), 2920(s), 1200(vs), 1170(w),1150(s), 1020(m), 880(vs), 840(s), 820(m).

^{1} H NMR (δ) : 0.6 (m, 20H, CH_3, CH), 2.4 (br.singlet, 4H, NH).

^{31} P NMR (δ) : 22.4 (t, 1P, PCl_2), 13.4 (d, 2P, $P(NHR)_2$), $^{2}J_{P-P} = 46.7$ Hz.

FAB Mass ($C_{12}H_{24}N_7P_3Cl_2$) : 430 found (M^+) = 430.

2.4 Synthesis of Octakis(Cyclohexylamino)Cyclotetraphosphazenes

2.4.1 Synthesis of 2,2,4,4,6,6,8,8-Octakis(cyclohexylamino) cyclotetraphosphazene (OCHEA)

To a stirred solution of octachlorocyclotetraphosphazene (2.0g, 4.0mmol) in benzene a mixture of cyclohexylamine (3.9g, 0.04mol) and triethylamine (3.9g, 0.04mol) was added drop wise. The mixture was stirred at room temperature for 8 hours and then refluxed at 80°C for 14 hours. The reaction mixture was brought to room temperature. Precipitated amine hydrochloride was separated by filtration. The solvent was stripped off under reduced pressure. The oily liquid obtained was subjected to silica gel column chromatography. Unreacted $N_4P_4Cl_8$ was removed by eluting with hexane. OCHEA can be obtained with 25% ethyl acetate / 75% hexane mixtures as the eluent (1.2g, 29%).

Melting point : 182°C.

Infrared (cm^{-1}) : 3245(m), 3360(m), 3340(m), 1240(s), 1450(s), 1110(s), 900(s).

^{1}H NMR (δ) : 1.5 (m, 88H, CH_3,CH), 3.0 (br.singlet, 8H, NH).

^{31}P NMR (δ) : 3.7 (s, 4P, $P(NHR)_2$).

FAB Mass ($C_{48}H_{96}N_{12}P_4$) : 966, found(M^+) = 966.

2.4.2 Synthesis of 2,2,4,4,6,6,8,8-Octakis(cyclopentylamino) cyclotetraphosphazene (OCPEA)

Octachlorocyclotetraphosphazene $N_4P_4Cl_8$,(2.0g, 4.0mmol) was taken in 100ml benzene. To this a mixture of cyclopentylamine (3.3g, 0.04mol) and triethylamine (3.9g, 0.04mol) was added dropwise. The mixture was stirred at room temperature for 12 hours and refluxed at 80°C for 8 hours. The mixture was brought to room temperature. Amine hydrochloride was filtered off. The solvent was removed under vacuum to get an oily liquid. The oily liquid was subjected to silica gel column chromatography. Initial fraction collected was found to be unreacted $N_4P_4Cl_8$. OCPEA was obtained by eluting with 25% ethylacetate and 75% hexane mixtures (1.3g, 36%).

Melting point : 136°C.

Infrared (cm^{-1}) : 3420(s), 1450(s), 1260(b),1170(s),1110(s), 900(b).

^{1}H NMR (δ) : 1.6 (m, 72H, CH_3, CH), 3.5 (s, 8H, NH).

^{31}P NMR (δ) : 3.8 (s, 4P, $P(NHR)_2$).

FAB Mass ($C_{40}H_{80}N_{12}P_4$) : 854 ; found (M^+) = 854.

2.4.3 Synthesis of 2,2,4,4,6,6,8,8-Octakis(cyclopropylamino) cyclotetraphosphazene (OCPRA)

To a benzene solution of octachlorocyclotetraphosphazene (2.0g, 4.0mmol) a mixture of cyclopropylamine (2.2g, 0.04mol) and triethylamine (3.9g, 0.04mol) was added dropwise. The reaction mixture was stirred continuously at room temperature for 12 hours and refluxed at 80°C for 14 hours. The mixture was brought to room temperature. Precipitated amine hydrochloride was separated by filtration. The solvent benzene was evaporated under reduced pressure to get an viscous liquid. Separating by silica gel column chromatography initially yielded unreacted $N_4P_4Cl_8$ in the first fraction. Continuous elution with 25% ethylacetate and 75% hexane gave OCPRA (0.9g, 34%).

Melting point : 130°C.

Infrared (cm^{-1}) : 3380(s), 3300(w), 3100(s), 2920(w), 1370(w), 1260(m), 1100(vs), 1020(w), 870(m), 820(m).

^{1}H NMR (δ) : 0.6 (m, 40H, CH_3,CH), 2.8 (br.singlet, 8H, NH).

^{31}P NMR (δ) : 6.7 (s, 4P, $P(NHR)_2$).

FAB Mass ($C_{24}H_{48}N_{12}P_4$) : 629 ; found (M^+) = 629.

2.5 Synthesis of Poly[bis(cyclicamino)phosphazenes]

2.5.1 Synthesis of Poly[bis(dichloro)phosphazene]

Hexachlorocyclotriphosphazene was purified by subliming $N_3P_3Cl_6$ at 0.01mm Hg maintained at 70°C. Highly purified $N_3P_3Cl_6$ (14.9g, 0.04mol) was thoroughly mixed with calcium sulphate dihydrate (3.0 mg) and tranferred into a thick-walled glass ampoule.

The tube was evacuated continuously for 2 hours and then sealed. The tube was then suspended in a thermo regulated oven maintained at 250°C for 14 hours. The tube was cooled to room temperature. The tube was broken into small pieces inside a glove bag and transferred to a Schlenk apparatus. Unpolymerized $N_3P_3Cl_6$ were recovered by refluxing the mixture in hexane under nitrogen atmosphere. After the complete removal of $N_3P_3Cl_6$, 100ml of THF was added to dissolve the polydichlorophosphazene. The residue was washed repeatedly with THF to get the title polymer $[NPCl_2]_n$ (5.0g, 34%).

2.5.2 Synthesis of poly[bis(cyclohexylamino)phosphazene] (CAPCP)

To a stirred solution of polydichlorophosphazene (2.8, 0.02mol) in THF a dilute solution of cyclohexylamine (4.9g, 0.05mol) and triethylamine (5.0g, 0.05mol) was added dropwise. The clear solution of polydichlorophosphazene became turbid indicating the formation of amine hydrochloride. The reaction mixture was stirred at room temperature for 6 hours and then refluxed at 70° C for 14 hours. The reaction mixture was cooled to room temperature. Amine hydrochloride was separated by filtering through a sintered funnel. Most of the solvent was evaporated *in vacuo* and the oily liquid obtained was poured into a large excess of ethanol. Reprecipitation was done three times to remove unreacted amines. The polymer was separated and vacuum dried (4.0g, 67.4%).

Infrared (cm^{-1}) : 3900(w), 2925(s), 1745(m), 1450(m), 1104(s), 888(m).

^{1}H NMR (δ): 1.6 (m, 22H, CH_3, CH), 3.0 (br.singlet, 2H, NH).

^{31}P NMR (δ) : 1.5 (br.singlet, 1P, $P(NHR)_2$).

Elemental analysis

2.5.3 Synthesis of poly[bis(cyclopentylamino)phosphazene] (CAPEP)

A mixture of cyclopentylamine (2.6g, 0.04mol) and triethylamine (3.1g, 0.04mol) in 100ml THF was added to a stirred solution of polydichlorophosphazene (1.8g, 0.02mol) in 200ml THF. The mixture was stirred at room temperature for 12 hours and then refluxed at 70°C for 24 hours. The mixture was brought to room temperature. Precipitated amine hydrochloride was separated by filtration. Most of the solvent was removed by evaporating under reduced pressure.The yellow oil obtained was poured into a large excess of ethanol affording a yellow solid. Reprecipitation was done by dissolving the polymer in minimum amount of THF and then pouring into excess ethanol. CAPEP was obtained as a yellow solid which was vacuum dried. (1.9g, 56%).

Infrared (cm^{-1}) : 3345(s), 2955(s), 2868(s), 1470(m), 1147(w), 902(m).

^{1}H NMR (δ) : 1.7 (m, 18H, CH_3, CH), 3.6 (br.singlet, 2H, NH).

^{31}P NMR (δ) : 2.1 (br.singlet, 1P, $P(NHR)_2$).

2.5.4 Synthesis of Poly[bis(cyclopropylamino)phosphazene] (CAPRP)

To a stirred solution of polydichlorophosphazene (5.4g, 0.05mol) in 100ml THF, a mixture of cyclopropylamine (5.3g, 0.1mol) and triethylamine (9.5g, 0.1mol) in 100ml THF was added dropwise. The mixture was stirred at room temperature for 12 hours and then refluxed at 70°C for 14 hours. The reaction mixture was brought to room temperature.Precipitated amine hydrochloride was separated by filtration. Removal of solvent *in vacuo* afforded a yellow viscous liquid which was poured into an excess of ethanol. Reprecipitation was done three times by dissoving the polymer in minimum amount of THF and then poured into excess ethanol. CAPRP obtained was filtered and vacuum dried (4.1g, 56%).

Infrared (cm^{-1}) : 2860(s), 1270(s), 1450(m), 950(s), 820(s).

^{1}H NMR (δ): 0.5 (m, 10H, CH_3, CH), 2.4 (br.singlet, 2H, NH).

^{31}P NMR (δ) : 1.8 (br.singlet, 1P, $P(NHR)_2$).

2.6 Results and Discussion

2.6.1 Synthesis and Characterization of Cyclotriphosphazene and Cyclotetraphosphazene Derivatives

In his pioneering study [54-61] on polyphosphazene derivatives Allcock from Pennsylvania state university has shown that it is advantageous to first study the reaction on small cyclic molecules before extending these to large macromolecules. This is particularly relevant in the field of polyphosphazenes since the variation in the structure and architecture of polyphosphazenes is achieved by the substitution of chlorines in polydichlorophosphazenes by the desired nucleophile such as an amine, alcohol or phenol.

2.6.2 Reaction of Chlorocyclophosphazenes with Cyclic Amines

The reactions of hexachlorocyclotriphospahzene ($N_3P_3Cl_6$) and octachlorocyclotetraphos phazene($N_4P_4Cl_8$) with the cyclic amines were carried out with the view to isolate the fully substituted derivatives. In view of the fact that synthesis of these polyphosphazenes involves substitution of chlorines on the macromolecule, it is advantageous to obtain information on reaction conditions etc., suitable for such substitution by first carrying out the same reaction on the small molecule cyclophosphazenes. We have accordingly first studied the reactions of hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) and octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) with cyclic amines, cyclohexylamine, cyclopentylamine, and cyclopropylamine with an intention to understand the reaction conditions for complete substitution of chlorines in these compounds (Figure 2.5.)

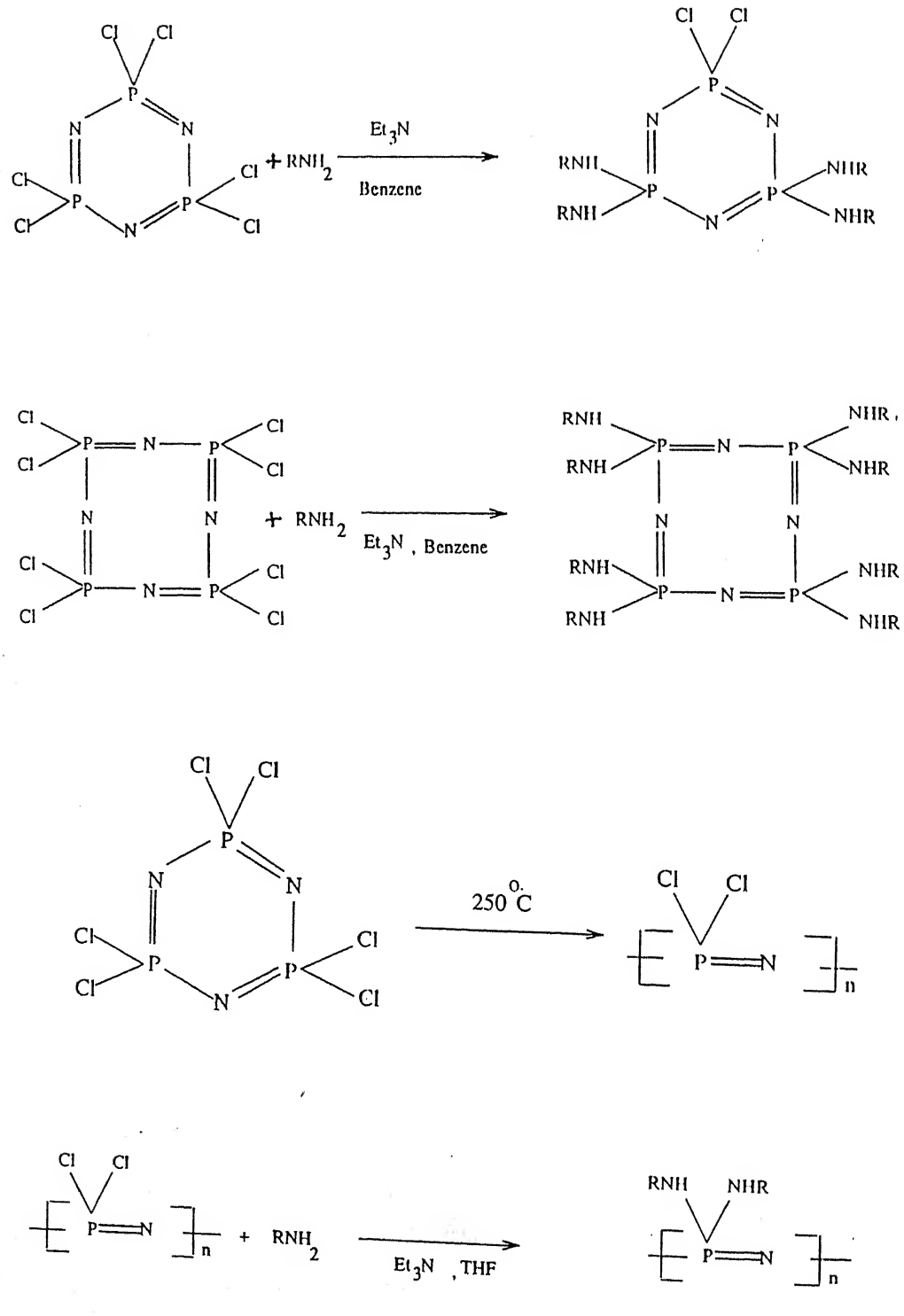

Figure 2.5: Synthetic Strategies for Preparing Cyclic Amino polyphosphazenes.

In a preliminary experiment inorder to judge when the replacement of the first chlorine is initiated, we carried out 1:1:1 ($N_3P_3Cl_6$: cyclopentylamine : triethylamine) in benzene at room temperature. Although some amount of unreacted $N_3P_3Cl_6$ was isolated, the major product obtained was the mono derivative $N_3P_3Cl_5(C_5H_9NH)$ which showed an AX_2 type of ^{31}P NMR spectrum (Figure 2.6).

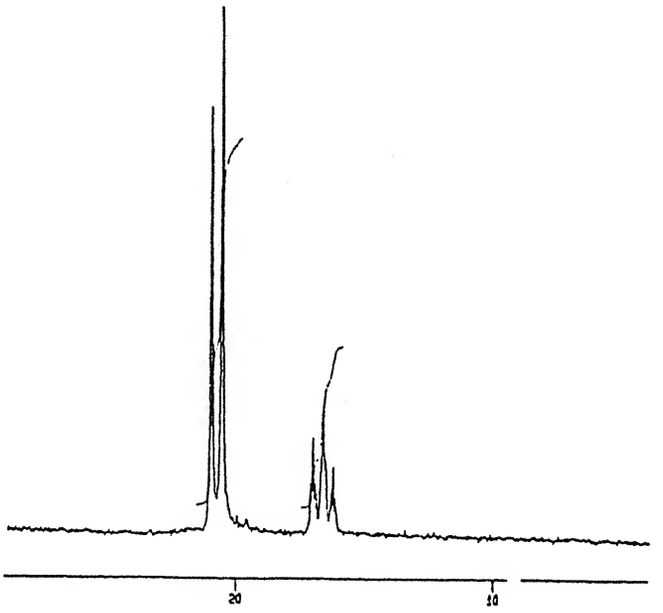

Figure 2.6: ^{31}P NMR Spectrum of $N_3P_3Cl_5(C_5H_9NH)$.

Similar product was isolated in the 1:2:2 reaction condition also. No attempt was made to study the complete replacement pattern as these have been well studied albeit with other amines. Under various conditions as shown in Table 2.3, the major product that was isolated by column chromatography was the tetrakis derivative $N_3P_3Cl_2(NHR)_4$. Presumably small amounts of hexakis derivative along with the other isomers of the tetrakis derivative as well as some pentakis derivative may have been formed in the reaction. But because of their very low yields as well as close Rf values in the TLC (at least for the other isomers of the tetrakis derivative) these could not be isolated in their pure forms. However ^{31}P NMR of the mixture shows the presence of a number of AX_2 multiplets clearly indicating their presence. (Figure 2.7)

Table 2.3: Experimental Details of Reaction of $N_3P_3Cl_6$ with Cyclic Amines

Amines	$N_3P_3Cl_6$ (moles)	RNH_2 (moles)	Et_3N (moles)	Solvent used	Yield %	Reaction condition	Product obtained
C_3H_5NH	0.014	0.086	0.086	C_6H_6	62.0	$8^a, 12^b$	d
C_5H_9NH	0.014	0.086	0.086	- do -	50.0	$12^a, 12^b$	d
- do-	0.003	0.003	0.003	- do -	22.3	$12^a, 0.6^c$	e
- do -	0.003	0.006	0.006	- do -	40.5	$12^a, 0.7^c$	e
- do -	0.003	0.009	0.009	- do -	23.8	$30^a, 0.42^c$	f
- do -	0.003	0.012	0.012	- do -	19.4	$24^a, 0.23^c$	f
- do -	0.003	0.014	0.014	- do -	29.3	$24^a, 0.70^c$	d
- do -	0.003	0.017	0.017	- do -	26.4	$24^a, 0.76^c$	d
- do -	0.003	0.029	0.029	- do -	28.6	$24^a, 0.82^c$	d
$C_6H_{11}NH$	0.006	0.034	0.034	THF	40.9	$12^a, 24^b$	d
- do -	0.014	0.086	0.086	CH_3CN	56.6	$12^a, 16^b$	d
- do -	0.014	0.086	0.086	C_6H_6	41.0	$12^a, 12^b$	d
- do -	0.006	0.057	0.057	$CHCl_3$	48.4	$6^a, 72^b$	d

[a] Reaction carried out at room temperature. [b] Reaction carried out at reflux conditions. [c] R_f Values obtained. [d] 2,2-gemdichloro-4,4,6,6-tetrakisderivatives. [e] Monosubstituted derivative. [f] structure could not be assigned.

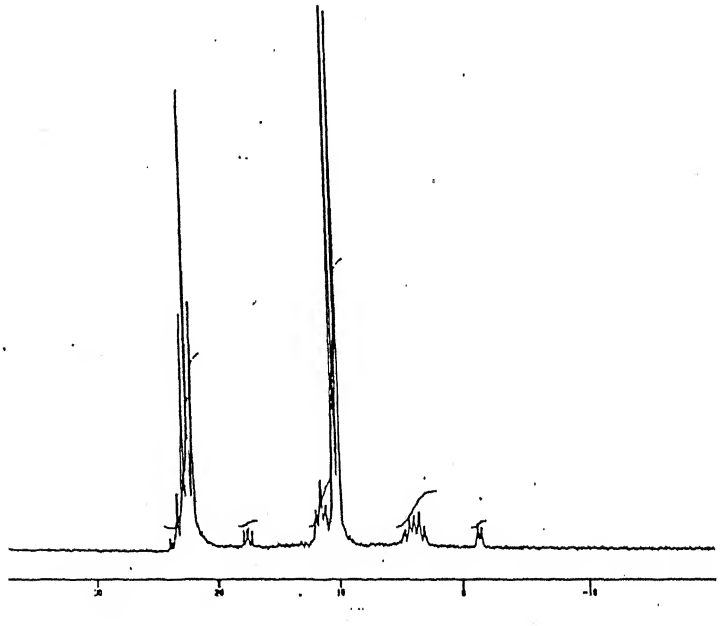

Figure 2.7: ^{31}P NMR Spectrum of Mixture of Derivatives.

2.7 Structural Characterization of $N_3P_3Cl_2(cyclicamine)_4$ and $N_4P_4(cyclicamine)_8$

The mass spectra of all these compounds DCHEA, DCPEA and DCPRA show strong parent ion peaks with the characteristic two chlorine pattern for the formula $N_3P_3Cl_2(NHR)_4$. The initial fragmentation in all these compounds proceeds by the loss of amino group rather than the chlorine dissociation. Typical FAB mass spectrum of the cyclopentyl amino derivative (DCPEA) is shown in Figure 2.8.

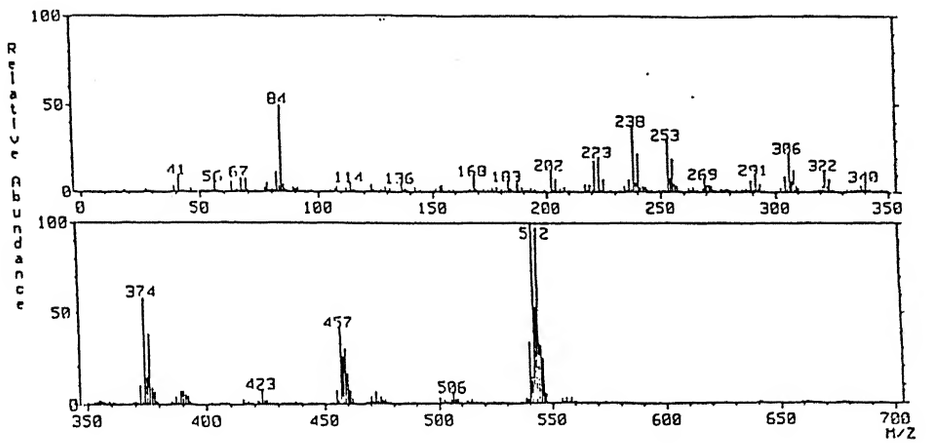

Figure 2.8: FAB Mass spectrum of DCPEA.

The structures of all the tetrakis products have been confirmed by multinuclear NMR, FAB mass and also by a representative X-ray analysis on DCHEA (*vide infra*). It has been shown that all the tetrakis derivatives have a geminal geometry. The tetra substituted cyclotriphosphazenes $N_3P_3Cl_2(NHR)_4$ can give rise to three different isomers (*see* Figure 2.9)

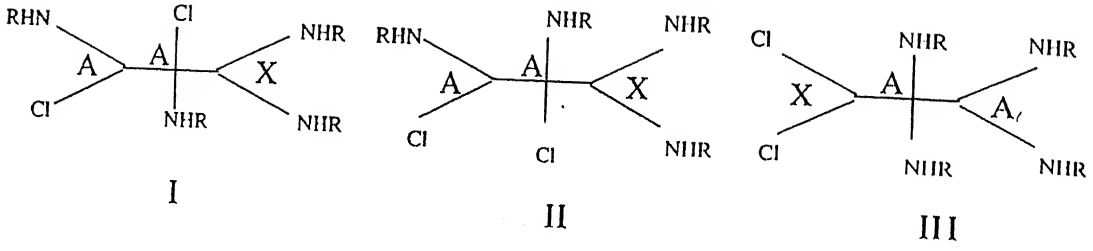

Figure 2.9: Possible Isomers of $N_3P_3Cl_2(NHR)_4$

The nongeminal regio isomers can itself have two stereo isomers cis and trans. As can be seen from the structures given, all of the three possible isomers would give rise to identical patterns in their phosphorus - 31 NMR spectrum. Thus I, II and III would show a AX_2 type of ^{31}P NMR spectrum. However, proton coupled phosphorus NMR can distinguish these possibilities. Thus in III ~~the~~ only X portion of the spectrum would be affected while in I and II both A and X portion would be affected.

The ^{31}P NMR spectra of DCHEA, DCPEA and DCPRA are all of the AX_2 type. An illustrative spectrum of the cyclopropylamino derivative is shown in Figure 2.10. In order to facilitate a comparison of the ^{31}P NMR chemical shifts observed in the present instance with that of the literature precedents several di and tetrachloro derivatives were searched. Table 2.4 summarizes the ^{31}P NMR data of these compounds.

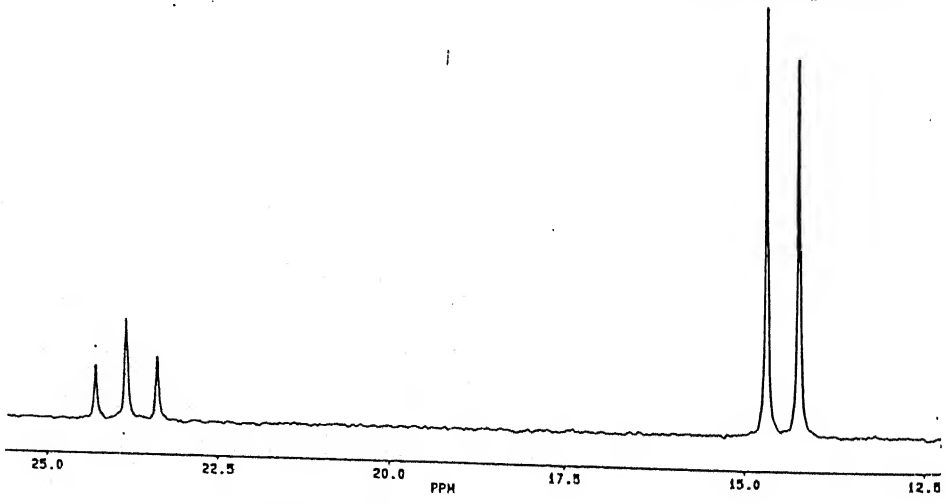

Figure 2.10: ^{31}P NMR spectrum of DCPRA.

Table 2.4: ^{31}P NMR Data of Selected Primary Amino Derivatives of $N_3P_3Cl_6$

Primary amino derivatives	δPCl_2 ppm	$\delta P(NRR')_2$ ppm	J_{p-p} Hz	Reference
$N_3P_3(NHPr^i)_4Cl_2$	22.2	9.4	49.4	14, 15
$N_3P_3(NHBu^t)_4Cl_2$	19.7	3.9	52.6	14
$N_3P_3(NHC_6H_4OMe-p)_4Cl_2$	23.6	2.1	50.8	20
$N_3P_3(NHCH_2CH_2Cl)_4Cl_2$	24.5	13.3	50.5	16
$N_3P_3(NH(CH_2)_3NH)_2Cl_2$	23.1	12.3	43.7	55
$N_3P_3(NHC_6H_{11})_4Cl_2$	22.6	9.9	49.4	present work
$N_3P_3(NHC_5H_9)_4Cl_2$	23.0	10.3	48.2	- do -
$N_3P_3(NHC_3H_5)_4Cl_2$	22.4	13.4	46.7	- do -

It is clear that the down field resonance is due to the PCl_2 group. Most chemical shift trends known in cyclotriphosphazene literature support this assignment. Secondly ^{31}P NMR carried out under proton coupled conditions indicate that this resonance is unaffected. The upfield resonance consequently has to be due to the $P(NHR)_2$ resonance. This also lends support to the assignment of the geminal structure to these products. The chemical shifts observed and the coupling constants are consistent with the geminal disposition of the amino substituent. Earlier literature studies have shown that where as with bulky amines such as t-butylamine and isopropylamine the substitution occurs by a geminal mode, with sterically less unencumbered amines such as methylamine or ethylamine the substitution proceeds *via* a non geminal mode. In view of our findings the cyclic amines behave analogous to the sterically demanding amines. It is likely that this preferential substitution occurs because of the proton abstraction mechanism as suggested by Shaw and coworkers (*see* Figure 2.11).

In the reactions of $N_3P_3Cl_6$ with amines an interesting pattern of regio selectivity is observed. Thus with primary amines both geminal and nongeminal pathways have been observed. Where as amines such as ammonia and t-butyl amine proceed *via* a geminal path way, amines such as ethylamine afford nongeminal products [15]. As the reactions of primary amines progress to higher degrees of substitution, the trisubsti-

tuted species which are isolated usually follow the same path way as their disubstituted precursors, however, in most cases the trisubstituted derivative is not isolated or isolated in low yields. By way of contrast, the tetrakis derivatives are generally geminally substituted. When nongeminal bis and tris products are formed, the trans isomer is the kinetically preferred product. The cis isomer, which is often also observed, presumably arises (in part atleast) from isomerization processes.

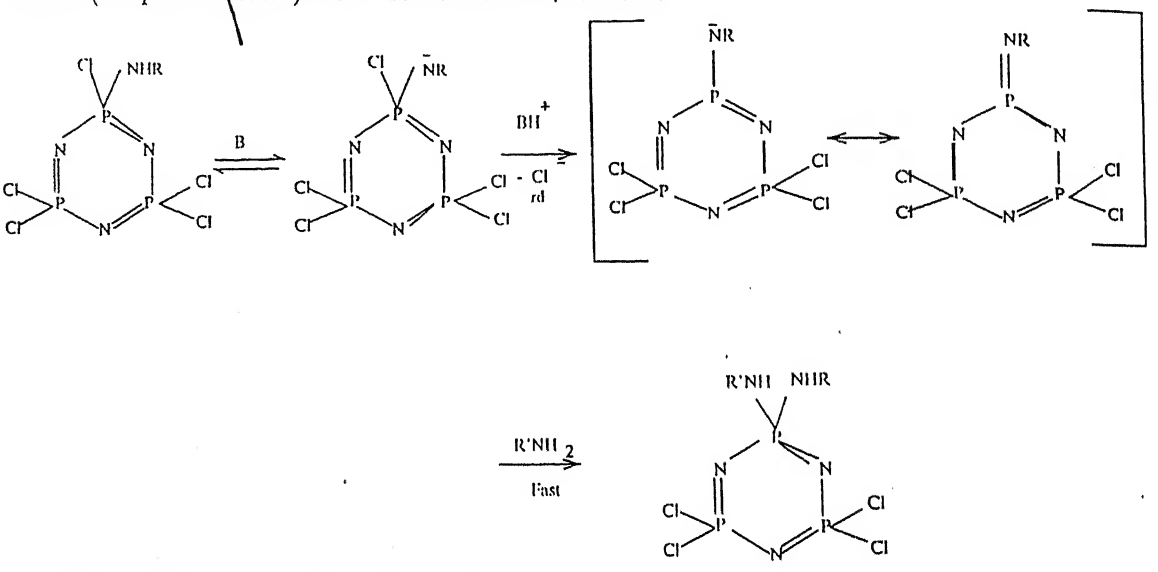

Figure 2.11: Proton Abstraction Mechanism.

However, β haloethylamines afford geminal products in diethyl ether as the solvent. Similar reaction with anilino derivatives proceed *via* a nongeminal path way. Inorder to account for the varying regio and stereo selectivities, Goldschmidt, Krishnamurthy, and their coworkers carried out detailed kinetic investigation[62,63]. The reaction kinetics for the formation of $N_3P_3Cl_5NRR'$ (which through light on other reaction pathways also) were found to be bimolecular. The reaction kinetics are bimolecular in polar solvents and show mixed second and third order (in amine) rate laws in non polar solvents (due to base catalysis). In polar solvents, the solvent assumes the base catalysis function. Activation parameters for several reactions are summarized in Table 2.5.

Table 2.5: Selected Activation Parameters for Cyclophosphazene Aminolysis Derivative.

phosphazene[a]	solvent	product $\Delta H^{\neq}$, kJ mol^{-1}	product $\Delta S^{\neq}$, J K^{-1} mol^{-1}
$N_3P_3Cl_5NHMe$	thf	2.9 ± 1.7	−205 ± 6
$N_3P_3Cl_5NMe_2$	thf	7.1 ± 2.1	−197 ± 8
$N_3P_3Cl_5NMe_2$	CH_3CN	20.7 ± 1.2	−128.0 ± 2.3
$N_3P_3F_5NMe_2$	CH_3CN	53.1 ± 1.7	−128.7 ± 3.2
$N_3P_3Cl_5NC_5H_{10}$	thf	12.1 ± 2.1	−188 ± 6
$N_3P_3Cl_5NHCMe_3$	thf	47.6 ± 2.1	−125.9 ± 6.0
$N_3P_3Cl_5NHCMe_3$	CH_3CN	20.3 ± 1.7	−205.7 ± 17.3
$N_4P_4Cl_7NHCMe_3$	CH_3CN	8.2 ± 2.0	−201.6 ± 42.2
$N_3P_3Cl_5NHPh$	CH_3CN	29.1[b]	−203.9[b]
$N_3P_3Cl_5NHC_6H_4OMe$	thf	21.9[b]	−261.7[b]
$N_3P_3Cl_5NHC_6H_4OMe$	CH_3CN	25.2[b]	−189.5[b]
cis-$N_3P_3Cl_4(NMe_2)_2$	thf	8.8 ± 0.5	−238 ± 8
trans-$N_3P_3Cl_4(NMe_2)_2$	thf	28.5 ± 1.3	−159 ± 8
trans-$N_3P_3Cl_4(NMe_2)_2$	CH_3CN	10.6 ± 1.4	−189.7 ± 3.2
2,4-$N_3P_3Cl_4(NHC_6H_4OMe)_2$	thf	29.1[b]	−278.2[b]
trans-2,4,6-$N_3P_3Cl_3(NMe_2)_3$	CH_3CN	14.0 ± 1.0	−196.4 ± 3.6
cis-2,2,4,6-$N_3P_3Cl_2(NMe_2)_4$	CH_3CN	21.0 ± 1.1	−217.2 ± 4.1

[a] Obtained in the reaction of the amine and the parent phosphazene.
[b] Error estimated as <5%.

Two possible path ways are envisaged for the bimolecular substitution. The difference between these two mechanisms revolves about the intermediacy of a neutral, five coordinate phosphorus Lewis acid-base adduct of the amine and the phosphazene. If the adduct is formed, a two step $S_N2(P)$ mechanism is followed, otherwise a one step, $S_N2(P)$ concerted process occurs (*see* Figure 2.12). It has been shown that the $\Delta H^{\neq}$ can be correlated with the formation of the five coordinate intermediate. Thus it can be seen clearly from the Table 2.5 that the eight membered ring has a very low $\Delta H^{\neq}$ in a number of reactions suggesting that it's flexibility allows it to adjust its geometry to suit the requirements of the S_N2 mechanism.

The possibility of geminal pathway is explained by a proton abstraction mechanism [64]. In this mechanism, proton abstraction at the amino substituent is followed by the formation of a three coordinate phosphorus. The next incoming nucleophile readily attacks this centre and relieves the steric strain of this phosphorus.

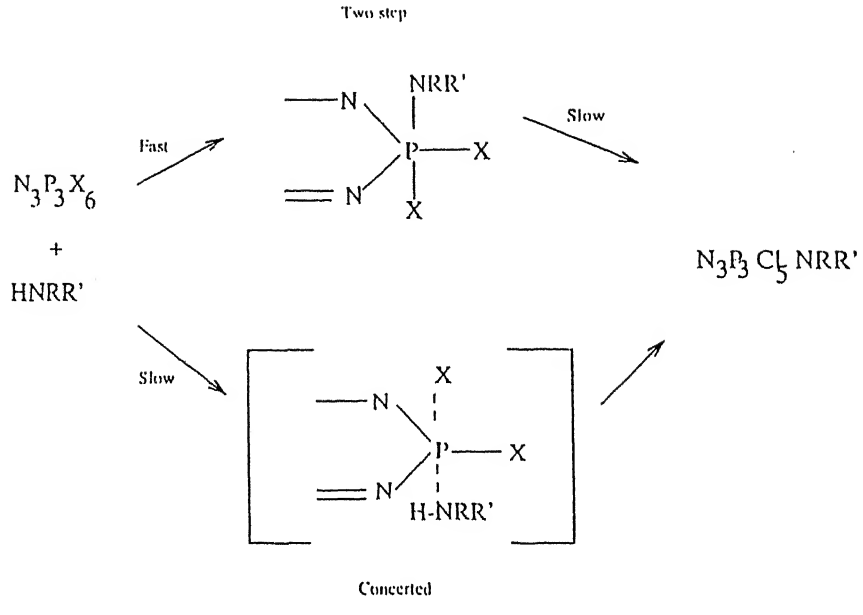

Figure 2.12: Possible Pathways for the Bimolecular Substitution.

All the cyclic amines investigated in the present study behave as sterically encumbered amines and prefer a geminal pathway. Also, it should be pointed out that in the reactions of $N_3P_3Cl_6$ with most primary amines after the bis stage of substitution rarely tris products have been isolated. And, a majority of primary amines afforded geminal products at the tetrakis stage. In addition all our reactions were carried out in the presence of a tertiary amine which would accelerate a proton abstraction mechanism induced reaction. Thus it is not surprising to observe almost exclusive geminal pathway at the tetrakis stage for the reaction carried out in the present study. We were unable to isolate hexakis derivatives in the reaction conditions as described in the experimental. It is likely that harsher sealed tube conditions may be required for full substitution.

In contrast to the reactions of cyclic amines with $N_3P_3Cl_6$, all the corresponding reactions with $N_4P_4Cl_8$ afford exclusively fully substituted derivatives $N_4P_4(C_6H_{11}NH)_8$ (OCHEA), $N_4P_4(C_5H_9NH)_8$ (OCPEA) and $N_4P_4(C_3H_5NH)_8$ (OCPRA). No partial substitution was detected in the reaction conditions as described in the experimental.

All the fully substituted derivatives are characterized readily by FAB Mass and Multinuclear NMR. An illustrative ^{31}P NMR spectrum of OCPRA is shown in Figure 2.13.

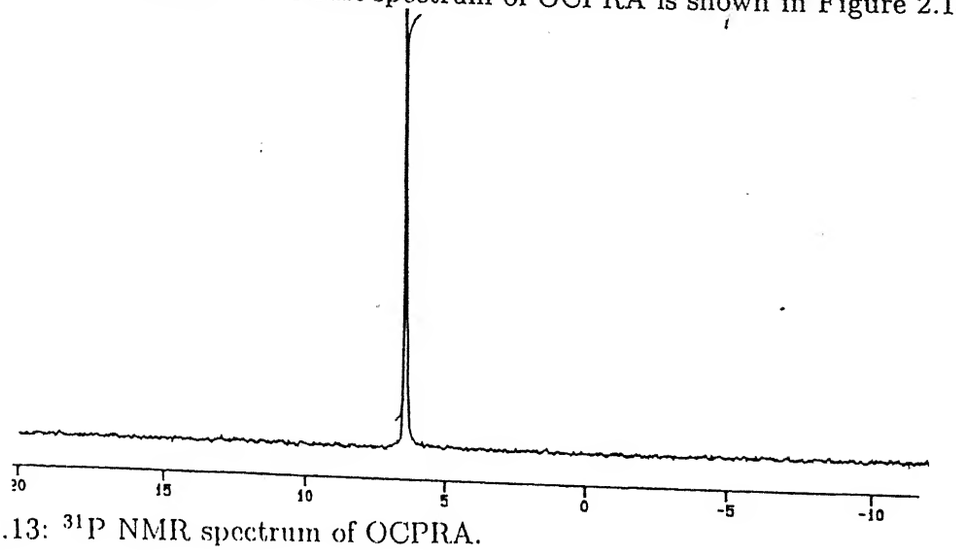

Figure 2.13: ^{31}P NMR spectrum of OCPRA.

The ^{31}P NMR of these compounds show a single line indicating complete substitution. These chemical shift values obtained are comparable with other fully substituted cyclotetraphosphazene derivatives. (Table 2.6). FAB mass of these derivatives shows parent ion peaks. Typical FAB mass spectrum of OCPEA is shown in Figure 2.14.

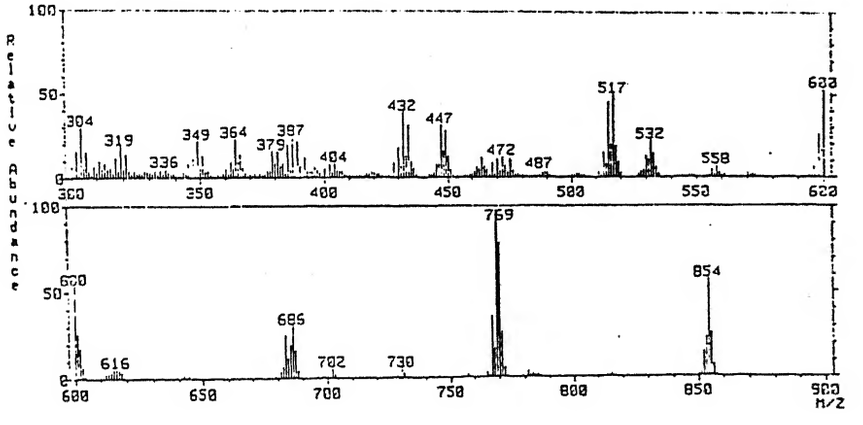

Figure 2.14: FAB Mass spectrum of OCPEA.

Table 2.6: ^{31}P NMR for Selected Primary Amino Derivatives of $N_4P_4Cl_8$

$N_4P_4(NHR)_8$	$\delta P(NR_2)_2$ ppm	Ref.
$N_4P_4(NHMe)_8$	11.1	65
$N_4P_4(NHEt)_8$	4.3	65
$N_4P_4(NHBu^t)_8$	-3.1	65,66
$N_4P_4(NHC_6H_{11})_8$	3.68	This work
$N_4P_4(NHC_5H_9)_8$	3.84	This work
$N_4P_4(NHC_3H_5)_8$	6.69	This work

2.7.1 X-ray Crystal Structure of 2,2-Dichloro-4,4,6,6-tetrakis (cyclohexylamino)cyclotriphosphazene (DCHEA)

The crystal parameters of the compound DCHEA are given in Table 2.7(a) . The molecule belongs to the triclinic space group P-1 and the structure has been solved by direct methods. The bond distance and bond angle data are given in Table 2.8. The ORTEP diagram of DCHEA is given in Figure 2.15. The molecule is nearly planar with one atom N (2) being out of the plane by 0.16$\AA$. The least square plane is given in Table 2.9. Since the molecule contains four geminal substituents of one type and two geminal substituents of other type there exists three types of ring P - N bond lengths (*see* Figure 2.16).

Table 2.7: Crystal Data for DCHEA (2.7a) and OCPRA (2.7b)

	Table 7a	Table 7b
formula	$P_3N_7Cl_2C_{24}H_{44}$	$P_4N_{12}C_{24}H_{48}$
fw	594.48	628.61
crystal size, mm	0.24 x 0.14 x 0.32	0.38 x 0.58x 0.66
crystal color	colorless	colorless
crystal mount	on fiber with silicone rubber	on fiber with silicone rubber
a,Å	11.2330(13)	12.433(3)
b,Å	11.4269(16)	20.484(4)
c,Å	13.4055(12)	12.645(3)
α,deg	72.211(10)	-
β,deg	72.150(9)	92.81
γ,deg	81.777(11)	-
V,Å^3	1557.3(3)	3216.5(13)
cell detn, refls	25	25
cell detn, 2θ range, deg	28-29	28-28.8
d(calcd), g cm^{-3}	1.268	1.298
space group	P-1	$P2_1/n$
Z	2	4
linear abs coeff, mm^{-1}	0.38	0.278
scan technique	$\theta - 2\theta$	$\theta - 2\theta$
2θ range, deg	4-40	4-50
h,k,l ranges	-10,10; 0,10; -11,12	-14, 14; 0, 24; 0, 15
std refl indices	-7 2 0; -4 -7 -5; -1 4 8	1, -6, 10; 2, 5, 9; 3, 4, 4
drift of stds,%	1.5	1.5
absorption range	0.840-0.999	0.89-0.90
refl meas	5055	5916
unique refls	2883	5617
R for merge	0.029	0.013
data with I>3σI	1935	3725
parameters refined	326	361
$R(F^2)$, $Rw(F^2)$	0.045, 0.065	0.043, 0.069
GOF	1.13	1.14
final diff map, eA^{-3}	-0.22(5), +0.44(5)	-0.34(6), +0.45(6)

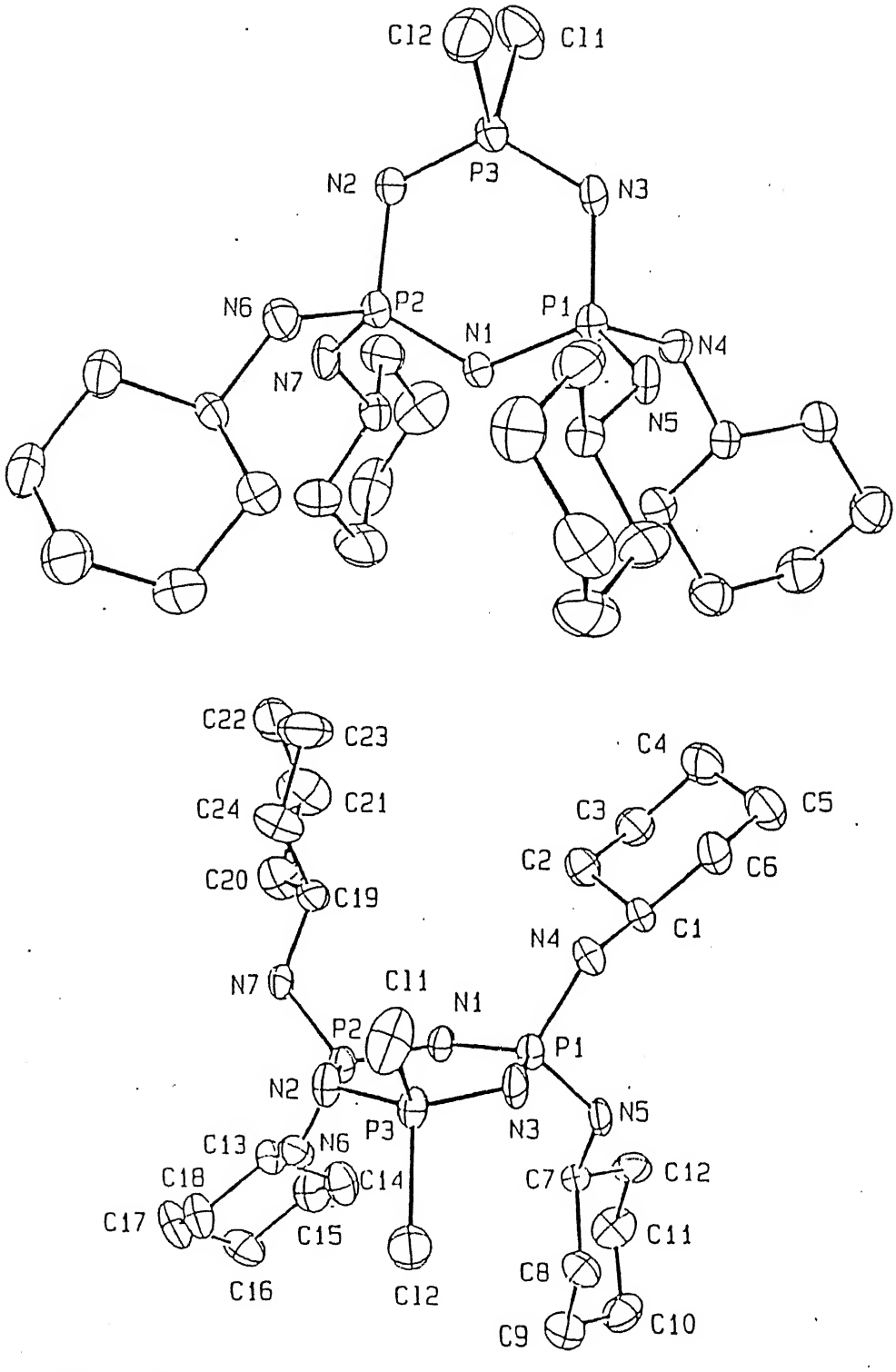

Figure 2.15: ORTEP diagrams of DCHEA

Table2.8: Selected Bond Distances $\AA$ and Bond angles ° in DCHEA

Selected bondlengths	P(1)-N(1)	1.589(5)	P(3)-N(2)	1.561(5)
	P(1)-N(3)	1.622(5)	P(3)-N(3)	1.553(5)
	P(1)-N(4)	1.632(5)	N(4)-C(1)	1.461(8)
	P(1)-N(5)	1.622(5)	N(5)-C(7)	1.468(8)
	P(2)-N(1)	1.581(5)	N(6)-C(13)	1.460(8)
	P(2)-N(2)	1.621(5)	N(7)-C(19)	1.472(8)
	P(2)-N(6)	1.641(5)	C(1)-C(2)	1.512(9)
	P(2)-N(7)	1.619(5)	C(2)-C(3)	1.518(11)
Selected bond angles	N(1)-P(1)-N(3)	114.2(2)	N(2)-P(3)-N(3)	121.3(3)
	N(1)-P(1)-N(4)	116.1(3)	P(1)-N(1)-P(2)	127.3(3)
	N(3)-P(1)-N(4)	101.9(3)	P(2)-N(2)-P(3)	120.8(3)
	N(4)-P(1)-N(5)	103.1(3)	P(1)-N(3)-P(3)	121.2(3)
	N(1)-P(2)-N(2)	113.7(2)	P(1)-N(4)-C(1)	126.8(4)
	N(1)-P(2)-N(6)	117.1(3)	P(1)-N(5)-C(7)	126.4(4)
	N(1)-P(2)-N(7)	107.5(2)	P(2)-N(6)-C(13)	127.7(4)
	N(2)-P(2)-N(6)	102.1(3)	N(4)-C(1)-C(2)	113.0(5)

The bond length 'a' is the shortest while the bond length 'b' is the longest viz., the bond lengths follow the order $b > c > a$. These bond length variations are rationalized in terms of different degrees of π bonding present with in the cyclophosphazene ring. The strongly electron withdrawing chlorine substituents contract the 'd' orbital at the phosphorus atoms and make them more compatible for π bonding with adjacent ring nitrogens. Thus the π bonding effects are maximum in the P - N bonds labelled 'a'.

There is less electron density available for the *pi* bonding component in the bond 'b'. Therefore the bond order 'b' increases in comparison with 'a'. The situation at 'c' is intermediate between 'a' and 'b'. This is reflected in the observed bond lengths. Similar trends are seen for the other known geminally substituted derivatives as shown in Table 2.9.

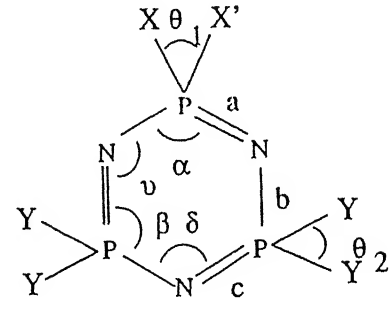

Figure 2.16: Three Types of Ring P-N bondlengths.

Table 2.9: Structural Parameters for the Compounds of General Formula $N_3P_3XX'Y_4$[a].

No.	Ring Substituents			Ring Conformation	P=N bond distances a, b, c	Bond angles			ref
	X	X'	Y			α,β	γ,δ	θ_1 θ_2	
1	$NPPh_3$	$NPPh_3$	Cl	Planar	1.642(5) 1.548(5) 1.575(5)	109.2(4) 120.8(3)	119.0(4) 117.5(0)	110.9(4) 99 .6(1)	67
2	$NHBu^t$	$NHBu^t$	Cl	Boat	1.61(1) 1.56(1) 1.58(1)	111.5(4) 119.2(5)	125.0(3) 119.1(6)	104.0(3) 99.3(2)	68
3	$NHSiMe_3$	$NHSiMe_3$	Cl	Planar	1.617(5) 1.551(3) 1.591(4)	111.6(3) 120.4(3)	125.0(3) 117.4(4)	105.9(4) 99.3(1)	69
4	NH_2	NH_2	F	Planar	1.597(5) 1.524(5) 1.564(5)	110.9 120.5	125.7 117.2	102.4 97.1	70
5	NH_2	NH_2	Cl	Nonplanar	1.616(4) 1.562(2) 1.573(2)	112.4(2) 119.9(1)	122.7(1) 118.6(2)	104.4(2) 101.2(2)	71
6	Cl	Cl	Ph	Slightlyboat	1.556(9) 1.609(9) 1.578(9)	120.7(4) 115.5(4)	121.0(5) 124.9(5)	104.4(5) 98.5(2)	72
7	Cl	Cl	NC_2H_4	Planar	1.558(3) 1.610(3) 1.584(3)	120.9(2) 116.3(1)	121.1(2) 124.2(2)	99.7(1) ng	73

Table 2.10: Distances to the Least Square Planes.

Plane no. 1

Distances(A) to the plane from the atoms in the plane.

P1	0.000(2)	P2	0.000(3)
P3	0.000(3)		

Distances (A) to the plane from the atoms out of the plane.

N1	0.009(5)	N2	0.177(6)
N3	-0.007(6)		

Plane no. 2

Distances(A) to the plane from the atoms in the plane.

P1	-0.000(2)	P2	-0.001(3)
P3	0.001(3)	N1	0.008(5)
N3	-0.007(6)		

Chi squared for this plane 3.795

Distances (A) to the plane from the atoms out of the plane.

N2	0.177(6)

Plane no. 3

Distances (A) to the plane from the atoms in the plane.

P2	0.000(3)	P3	0.000(3)
N2	0.000(8)		

Plane no. 4

Distances (A) to the plane from the atoms in the plane.

P1	0.005(2)	P2	-0.013(3)
P3	-0.012(3)	N1	0.007(5)
N2	0.160(6)	N3	-0.008(6)

Chi squared for this plane 857.932

Dihedral angle between planes A and B

A	B	Angle(deg)
1	2	0.04(10)
1	3	13.1(4)
1	4	0.41(7)
2	3	13.1(4)
2	4	0.41(7)
3	4	12.6(4)

The endocyclic bond angles at phosphorous in a ring are the largest at P3 (121.3°)(3) smallest at P1 and P2. The endocyclic angles at nitrogen are the smallest at N(2) and N(3) and largest at N(1). Such variation of bond angles $\alpha > \beta$ and $\delta < \gamma$ is also observed for the other geminal tetra substituted derivatives [68,70]. Similar bond angle variations have also been observed for spirocyclic derivatives [37-46].

2.7.2 X-ray Crystal Structure of Octakis(cyclopropylamino) cyclotetraphosphazene (OCPRA)

There are very few known x-ray structures of fully substituted amino cyclotetraphosphazenes. In fact to the best of our knowledge there are only two other x-ray structures known apart from the present example OCPRA. viz., $N_4P_4(NMe_2)_8$ and $N_4P_4(NC_4H_8)_8$. The crystal parameters for the compound OCPRA are summarized in Table 2.7b. The main feature of the structure is the presence of two crystallographically independent molecule each located on an inversion center. The ORTEP diagram of the two molecules are given in Figure 2.17. An important feature of the structure is the distortion of planarity in the cyclotetraphosphazene ring. Thus in molecule 1 with respect to plane of P1, P2, P1a and P2a the atom N(2) is out of plane by -0.875(3)$\AA$, while the atom N(1) is out of plane by +0.610(3)$\AA$. In comparison in molecule 2 with reference to the plane P11, P12, P11b and P12b the atoms N11 and N12 are out of plane by 0.180(3) and 0.553(3)Å. Such distortion of planarity is quite common in cyclotetraphosphazene systems. Thus $N_4P_4Cl_8$ it self exist in a boat and chair conformation, while $N_4P_4(NMe_2)_8$, $N_4P_4Me_8$ and $N_4P_4(NC_4H_8)_8$ are all puckered. The bond distance and bond angle data are given in Table 2.11.

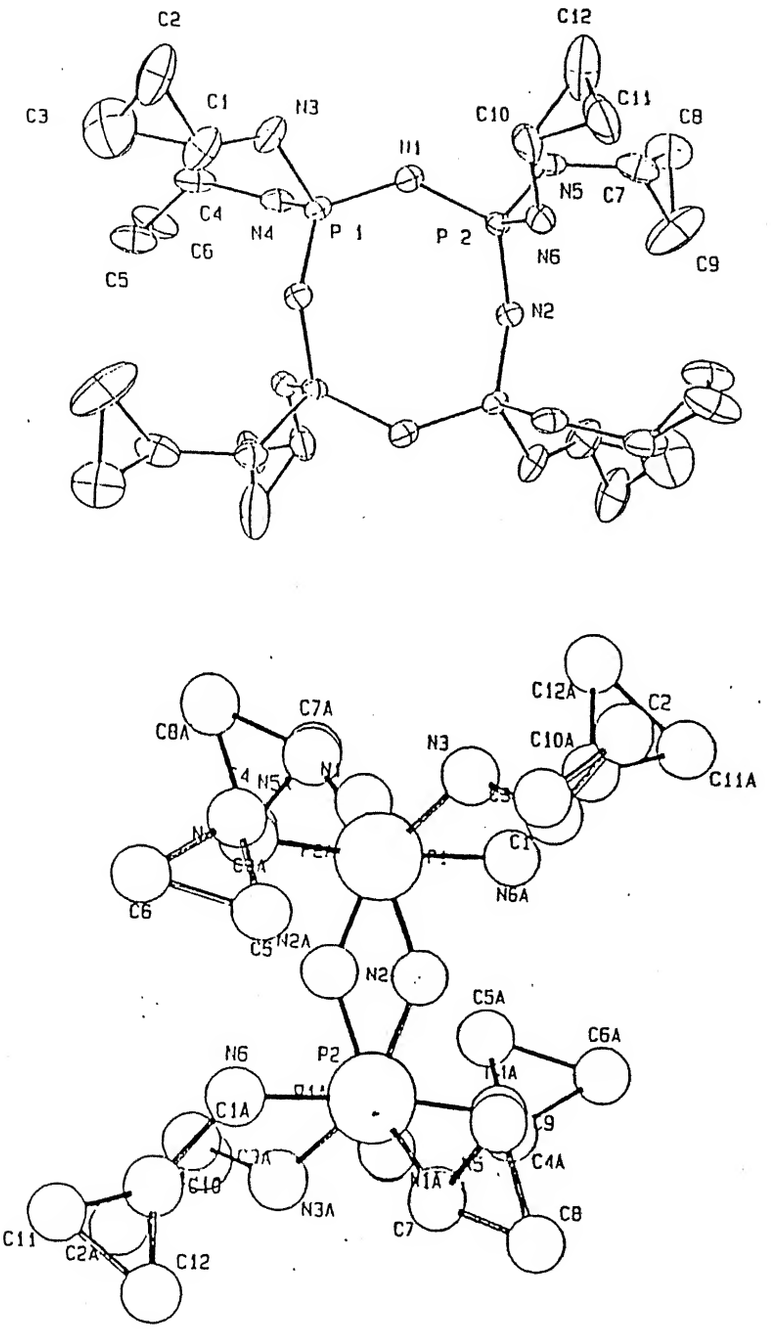

Figure 2.17: X-ray structures of OCPRA.

Table 2.11: Selected Bond DistancesÅ and Bond Angles° for OCPRA.

Selected bondlengthsÅ.			
P(1)-N(1)	1.582(3)	P(12)-N(12)	1.588(3)
P(1)-N(2a)	1.569(3)	P(12)-N(15)	1.646(3)
P(1)-N(3)	1.659(3)	P(12)-N(16)	1.665(3)
P(1)-N(4)	1.678(3)	N(3)-C(1)	1.448(6)
P(2)-N(1)	1.583(3)	N(4)-C(4)	1.442(5)
P(2)-N(2)	1.586(3)	N(5)-C(7)	1.430(5)
P(2)-N(5)	1.643(3)	N(6)-C(10)	1.431(5)
P(2)-N(6)	1.663(3)	N(13)-C(13)	1.434(5)
P(11)-N(11)	1.582(3)	N(14)-C(16)	1.441(5)
P(11)-N(12b)	1.579(3)	N(15)-C(19)	1.435(5)

Selected bond angles.			
N(1)-P(1)-N(2)	122.0(16)	N(11)-P(11)-N(12b)	119.9(16)
N(1)-P(1)-N(3)	105.5(17)	N(11)-P(11)-N(14)	103.2(16)
N(1)-P(1)-N(4)	103.5(17)	N(12b)-P(11)-N(14)	110.4(16)
N(2)-P(1)-N(3)	105.8(17)	N(12b)-P(11)-N(14)	101.5(16)
N(1)-P(2)-N(2a)	119.3(16)	N(13)-P(11)-N(14)	107.4(16)
N(1)-P(2)-N(5)	101.0(16)	N(11)-P(12)-N(12)	118.7(16)
N(1)-P(2)-N(6)	113.5(17)	N(11)-P(12)-N(15)	101.9(16)
N(2a)-P(2)-N(5)	105.7(16)	N(11)-P(12)-N(16)	112.8(16)
N(5)-P(2)-N(6)	107.1(17)	N(15)-P(12)-N(16)	106.3(17)

The endocyclic bond angles are all equal with average bond lengths 1.582Å(11). This value compares well with other amino substituted derivatives whose bond lengths are known. The exocyclic bond lengths are expectedly longer 1.661Å(18). The bond angles P - N - P 133°(4), NPN 120 °(2) are un exceptional. The exocyclic N - P - N bond angle averages to a nearly tetrahedral value 107°(6).

2.8 Polyphosphazenes Containing Cyclicamino Substituents

Thermal polymerization of hexachlorocyclotriphosphazene yields the linear high polymer poly(dichlorophosphazene), which can undergo nucleophilic replacement of the chlorine atoms to afford poly(organo)phosphazenes. Polyphosphazene polymers provide excellent oppurtunity for exploring the effects of changes in side group structure

on the physical property of the macromolecules [74]. Depending on the bulkiness of the side group the skeletal flexibility changes, thus altering the glass transition temperature (*see* Figure 2.18.)

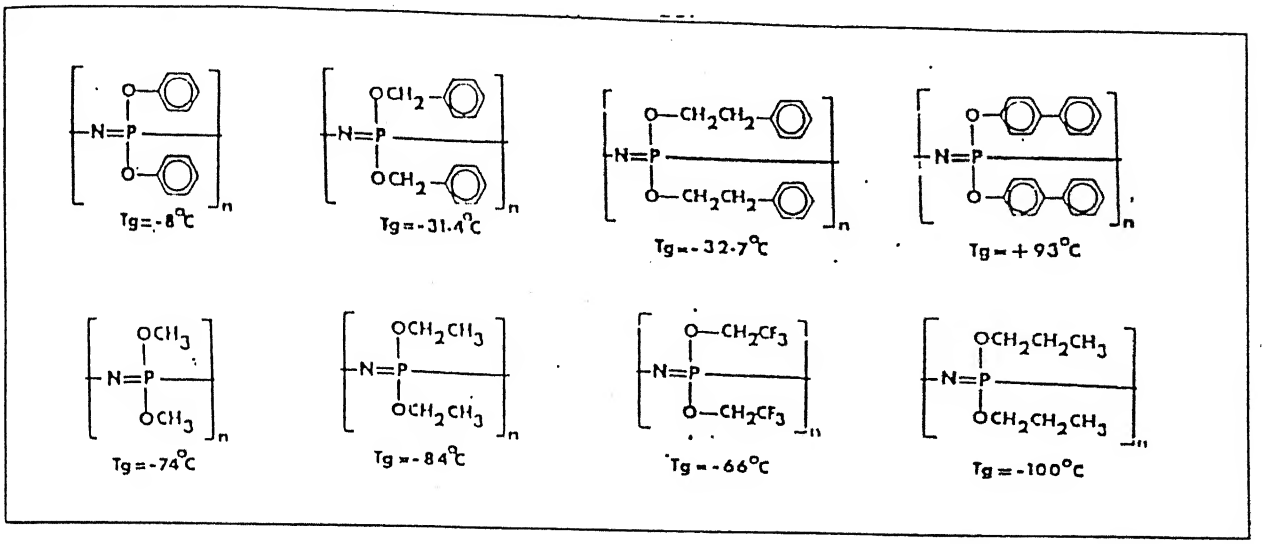

Figure 2.18: Variation of Glass Transition Temperature (Tg) with Polyphosphazene Side Group Structure.

The phosphazene backbone it self appears to be hydrophilic due mainly to the presence of the nitrogen lonepair electrons and their ability to form hydrogen bonds to water molecules. However, the overall hydrophilic character is determined by the side groups and by the degree to which they shield the skeleton. For example side groups such as $-NHCH_3$, $-OCH_2CH_2OCH_2CH_2OCH_3$, glucosyl and glyceryl which are themselves hydrophilic, generate ~~solubility of the~~ polymer, in water. Methyl side groups are sufficiently small that they do not shield the backbone nitrogen atoms: thus, methyl phosphazene polymers are hydrophilic without being water soluble. On the other hand, side groups such as OCH_2CF_3 or OPh which are both hydrophobic and bulky enough to shield the skeleton, generate strong water repellency and confer solubility in specific organic solvents.

Polydichlorophosphazene prepared by the thermal polymerization of hexachlorocyclotriphosphazene, was allowed to react with cyclic amines in presence of the hydrogen chloride scavenger triethylamine to afford cyclic amino polyphosphazenes CAPCP, CAPEP and CAPRP. These polymers were isolated as white powders that were soluble in polar organic solvents such as THF and acetone. In contrast CAPRP was soluble only in hot THF. Although the polymers initially are soluble, prolonged storage reduces solublity because of crosslinking reactions that can take place because of the presence of unreacted P - Cl groups in the polymer. Such a phenomenon is well known for the more reactive cyclotetraphosphazene derivatives. Polymers CAPCP, CAPEP and CAPRP were characterized by ^{31}P NMR , ^{1}H NMR, Infrared spectroscopy, differential scanning calorimetry and Thermo gravimetric analysis. The data obtained from these studies are summarized in Table 2.12. In addtion the molecular weight of the polymers were determined by dilute solution methods. The infrared spectra of the polymers contained intense absorptions at 1250-1300cm^{-1}. These are characteristic of P=N skeletal vibrations. The ^{1}H NMR were consistent with the assigned structures. As shown in the ^{31}P NMR (*see* Figure 2.19) of the cyclopentylamine derivative (CAPEP) the major component has to be due to the completely substituted derivative. Comparison of the chemical shifts of some known primary amino substituted polyphosphazene shows a remarkable similarity in trends. Dilute solution viscosity studies carried out on the polymer revealed that the intrinic viscosity is 11.8 cc/g (CAPCP) and 34.7 cc/g (CAPEP). Table 2.13 summarizes the data on η relative, η specific and η reduced at different concentration of CAPEP.

Table 2.13: Dilute Solution Characterization of CAPEP.

No.	Relative Viscosity η_{rel}	Specific Viscosity η_{sp}	Reduced Viscosity η_{red}	Concentration g/100ml
1	1.480	0.480	48.0	1.000
2	1.2095	0.2095	41.8	0.500
3	1.100	0.100	40.0	0.25
4	1.0395	0.0395	31.6	0.1250
5	1.0222	0.0222	35.5	0.0625
6	1.0110	0.0110	35.2	0.0312

2.8.1 Thermal studies

The glass transition temperature (Tg) of a polymer is believed to be a measure of the reorientational freedom of the macromolecular chain. The Tg values for the polymers CAPCP, CAPEP and CAPRP together with the related primary amino derivatives are shown in Table 2.12. DSC studies indicate that these polymers have glass transition temperature 219°C (CAPCP), 217°C (CAPEP) and 92°C (CAPRP) respectively. This indicates that these cyclic amino polyphosphazene derivatives are less flexible than other primary amino derivatives. The cyclic three membered, five membered and six membered side groups reduce the torsional mobility of the chain and hence the Tg is high. The lower glass transition temperature for CAPRP can be ascribed to the less bulky nature of the cyclopropyl group which imparts greater torsinol mobility of the chain. Thermal gravimetric analysis indicate that CAPCP (*see* Figure 2.20) decomposes by three step process leaving 33.73% char yield at 700°C where as CAPEP and CAPRP under goes multi step decomposition giving char yield 38.37% and 10.38% respectively.

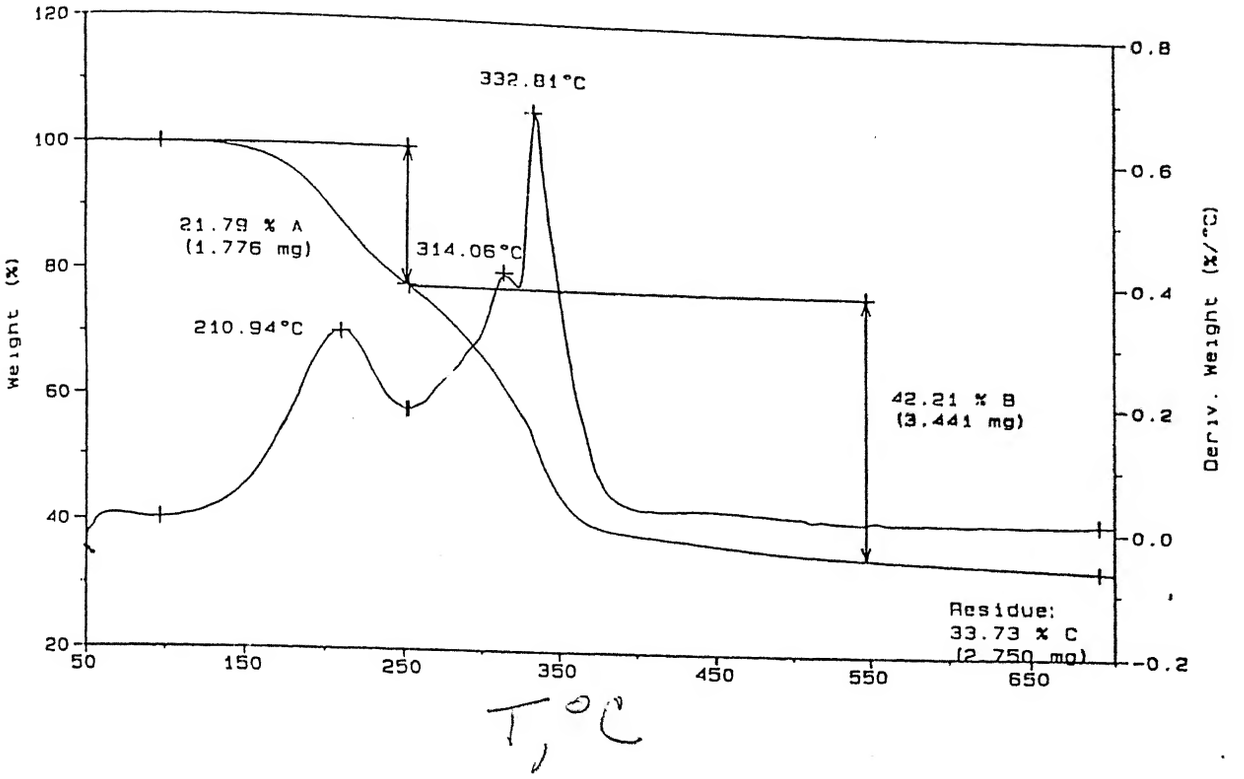

Figure 2.20: Thermogram of CAPCP.

2.9 Conclusions

1. New types of cyclo and polyphosphazenes that bear cyclic amine side groups (cyclopropylamine, cyclopentylamine and cyclohexylamine) have been synthesized.

2. The cyclic amines investigated in the present study afforded geminal dichlorotetrakis(cyclicamino)derivatives (DCHEA, DCPEA and DCPRA) with $N_3P_3Cl_6$, and fully substituted derivatives (OCHEA, OCPEA and OCPRA) with $N_4P_4Cl_8$.

3. X-ray studies of $N_3P_3Cl_2(NHC_6H_{11})_4$ (DCHEA) confirmed the near planar cyclotriphosphazene ring with one atom N(2) being out of plane by $0.16\mathring{A}$, where as the structural studies on $N_4P_4(NHC_3H_5)_8$ (OCPRA) showed that the cyclotetraphosphazene ring is puckered.

4. The poly[bis(cyclicamino)phosphazenes] CAPCP, CAPEP and CAPRP all contained small amount of residual chlorines. Attempts to substitute these chlorines by amines did not succeed.

5. The glass transition temperatures of these polymers CAPCP, CAPEP and CAPRP are higher than other primary amino substituted derivatives. This indicates the bulky nature of the cyclic amino side groups, which reduces the torsional mobility of the polymer backbone.

6. Further investigation on the synthesis of partially substituted derivatives using methoxide, trifluoroethoxide and phenoxide side groups remains an important field of research.

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Chapter 3

Pendant Cyclotetraphosphazene Monomers and their Homo and Copolymerization

3.1 Introduction

Linear phosphazenes containing P=N backbone in the polymer chain are now quite well known, and form one of the most important classes of inorganic polymers [1-6]. This aspect has been dealt in detail in chapter one of the thesis. However, in contrast studies on polymers containing cyclophosphazene as a pendant group on an organic polymer are relatively few [4-7]. These polymers should be especially interesting since these can be viewed as organic polymers with unusual side chain substituents where the substituents can be expected to render the polymer with special and probably unique properties [8,9]. The development of this area of polyphosphazenes requires the synthesis of suitable cyclophosphazene monomers that contain a polymerizable functionality.

Allen and coworkers have first initiated a programme of research [4-7] directed towards the synthesis of cyclotriphosphazene containing monomers. The monomers studied by Allen and coworkers and the synthetic methodology involved in their preparation is summarized in Figure 3.1.

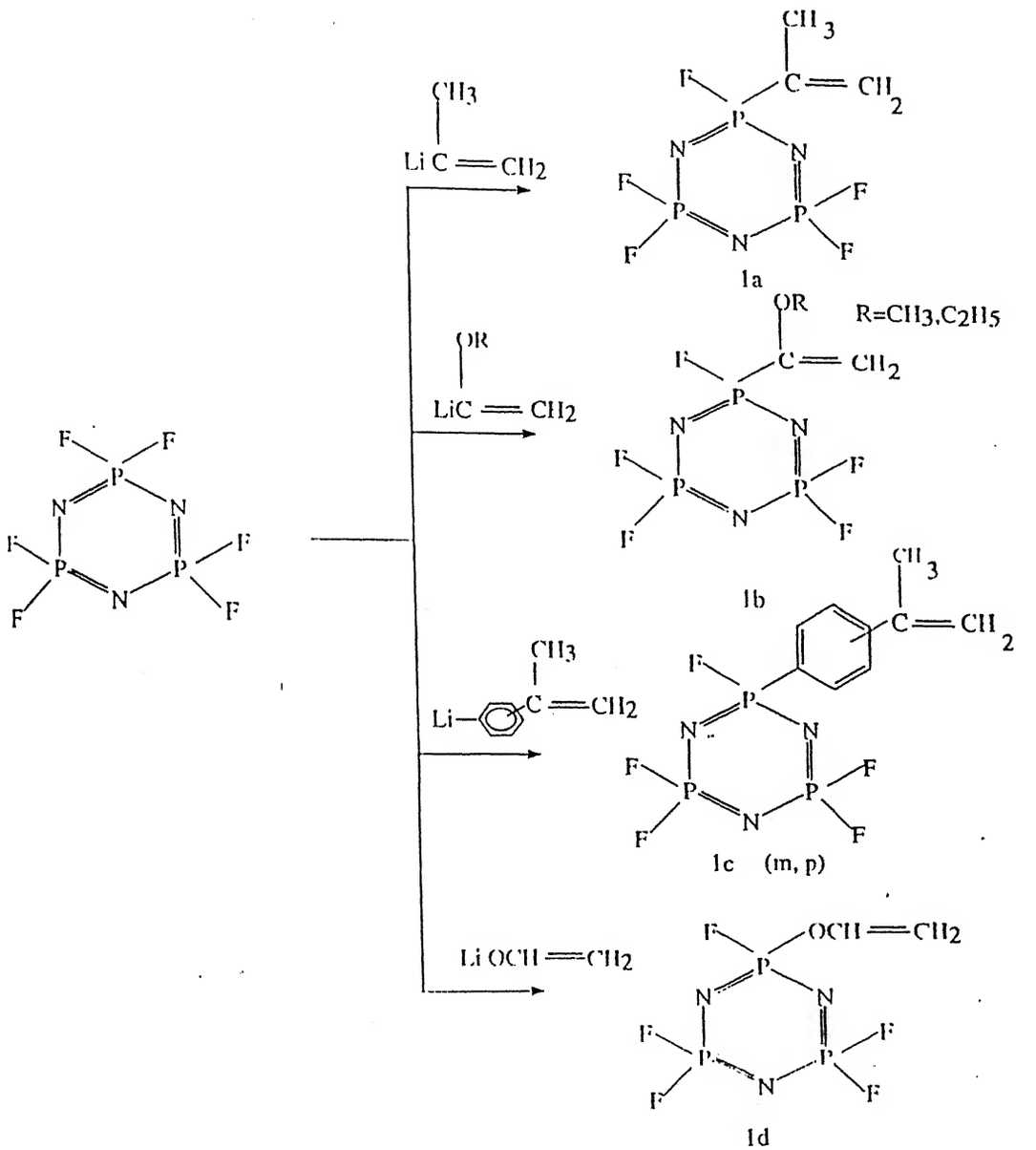


Figure 3.1 Examples of Pendant Cyclotriphosphazene Monomers.

The monomers prepared by Allen and coworkers are 2-(2-propenylpentaflourocyclotriphosphazene) [10], 2-(α-ethoxyvinyl)pentafluorocyclotriphosphazene [11], and ((α-methylethynyl)- phenyl)pentafluorocyclotriphosphazene [12]. These compounds have been synthesized by making use of well developed substitution chemistry of halogenocyclophosphazenes [13-14].

Since reactions of chlorocyclophosphazenes with alkyl or aryl lithium reagents is known to afford primarily ring degraded products [15], Allen and coworkers preferred to use hexafluorocyclotriphosphazene ($N_3P_3F_6$) as a starting material for the synthesis of 1a, 1b, 1c, and 1d. These monomers however, could not be homopolymerized under free radical conditions. It was felt that the cyclophosphazene ring functions as a σ electron withdrawing substituent [16] and hence depletes the electron density from the vinyl group, retarding the rate of polymerization. It was also possible that steric factors might be equally responsible for the sluggish reactivity of 1a, 1b, 1c, and 1d, since these are α-α disubstituted olefins which are known to be difficult to polymerize [11]. However, Allen and coworkers found that these cyclophosphazene monomers could be copolymerized with certain organic monomers such as styrene and methyl methacrylate giving rise to interesting hybrid organic-inorganic polymers.

More recently Inoue and coworkers [17] and Selvaraj and Chandrasekhar [18] have shown that cyclotriphosphazene containing 2'-(4'-vinyl-4- biphenyloxy) substituent $N_3P_3Cl_5(C_{14}H_{11}O)$ (CPHVB) undergoes both homopolymerization as well as copolymerization. This monomer was prepared with the view to overcome the steric and electronic factors that retarded homopolymerization in Allen's monomers. Thus in CPHVB the vinyl group is sterically unencumbered and also insulated from the cyclophosphazene ring by the presence of two biphenyl units. Interestingly the copolymers of CPHVB with acrylate monomers have good thermal stabilities with char yields of about 60% at 600°C; also it was found that only small amounts of CPHVB are required

to promote high thermal stabilities [6]. All these copolymers were flame retardant as shown by simple flame tests. Interestingly Inoue and coworkers were also able to prepare novel polymer electrolytes with good lithium ion conductivities (10^{-5} S cm^{-1}) based on these type of systems (2d and 2e in Figure 3.2) [19-20].

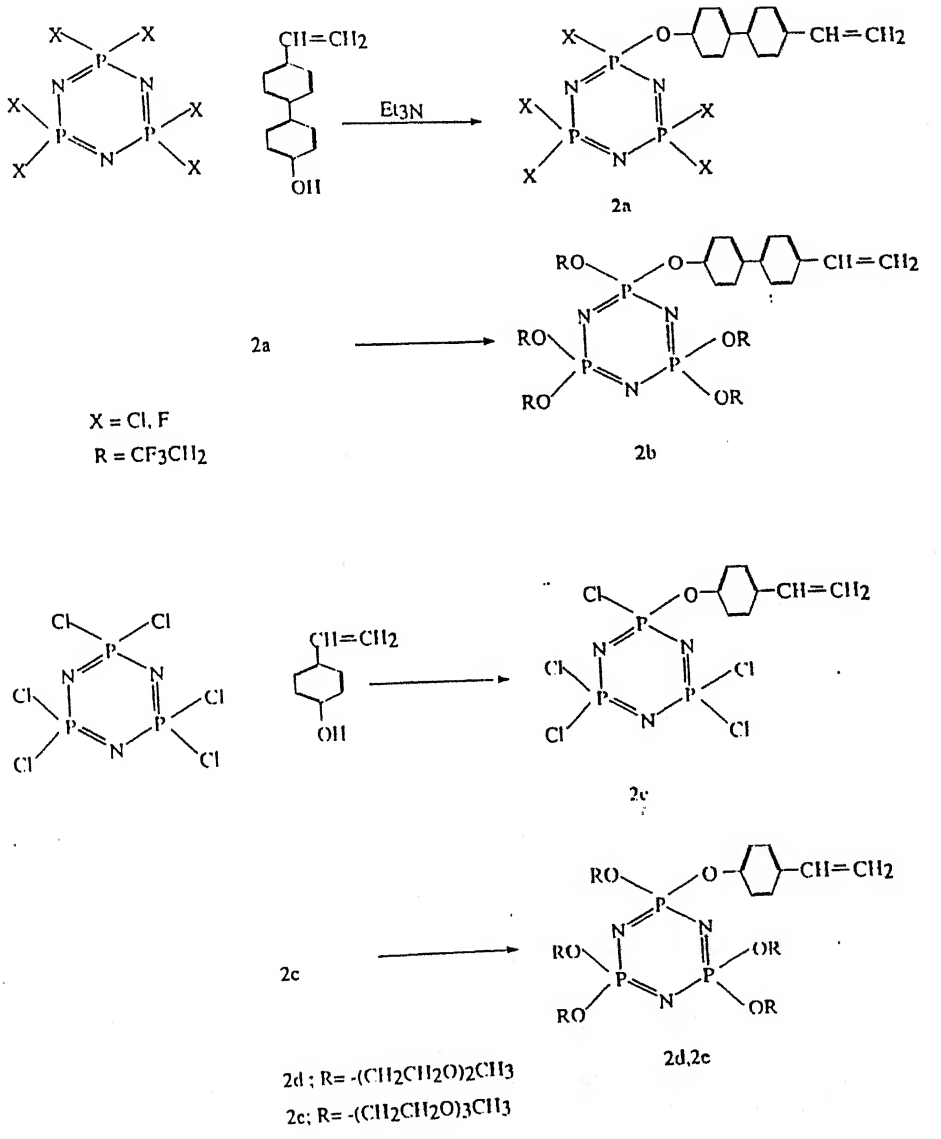


Figure 3.2 Pendant Cyclotriphosphazene Monomers Having an Insulating Groups.

Figure 3.2 summarizes the synthetic methodology involved in the preparation of these monomers. Inoue and coworkers have also prepared cyclophosphazene substituted vinylstyrene derivatives as shown in Figure 3.2. All of these monomers could be homo and copolymerized.

In another variation Inoue and coworkers have also succeded in the synthesis of new methacrylic substituent containing cyclophosphazenes according to Figure 3.3 [21,22].

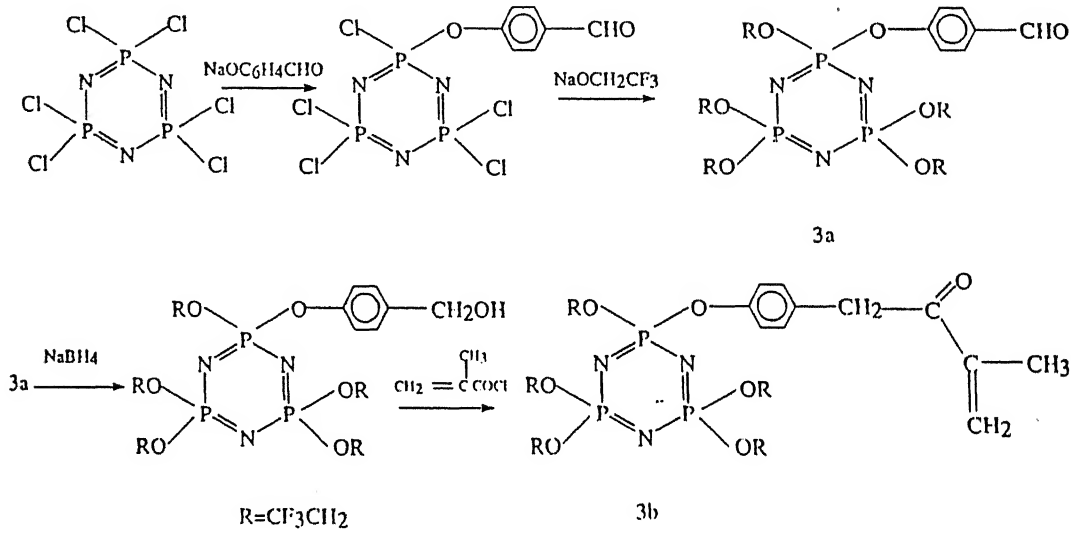


Figure 3.3 Example for a Pendant Cyclotriphosphazene Monomer Containing a Methacrylic Group.

Other types of cyclophosphazene monomers such as $N_3P_3Cl_5(NHCH_2CH=CH_2)$ have also been prepared [23] but could not be homopolymerized because of the auto inhibitory effect of the allylic monomer. Although Allen and coworkers prepared a number of vinyloxy cyclophosphazenes by the reaction of enolate anions of acetalde-

hyde with $N_3P_3F_6$, there are no detailed reports on their polymerization behaviour.

It is clear from the above discussion that there have been very limited studies on cyclotriphosphazene substituted vinyl monomers and none on cyclotetraphosphazene containing monomers. It was interesting to see if the synthetic methodologies that were successful with $N_3P_3Cl_6$ could be applied to $N_4P_4Cl_8$ as well. Secondly it was interesting to compare the properties of the polymer obtained from cyclotri and tetra phosphazenes. In view of this we have investigated the assembly of three different types of cyclotetraphosphazene containing organic monomers, $N_4P_4Cl_7(C_{14}H_{11}O)$ (TETHVB), $N_4P_4Cl_7(C_9H_7O_3)$ (TETQMA) and $N_4P_4Cl_7(C_8H_7O)$ (TETPHS). Due to the instability of the monomers only $N_4P_4Cl_7(C_{14}H_{11}O)$ was studied for its homo and copolymerization behaviour. The synthesis of these monomers and polymerization behaviour of TETHVB is discussed in this chapter.

3.2 Experimental

3.2.1 Materials

Octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) (Nippon soda, Japan) was recrystallized repeatedly from pentane to a constant melting (123°C) crystalline solid. 4-Hydroxy-4'-vinylbiphenyl (HVB)[24], hydroquinonemonoacrylate (HQMA) [25], 4-hydroxy styrene (PHS) [26-27] were prepared by literature procedures and are given below. All organic solvents were purified and dried by standard procedures [28]. Styrene (Fluka, Switzerland) was washed with dilute sodium hydroxide solution followed by distilled water to remove tertiary butyl catechol inhibitor. The dried organic monomer was then distilled at reduced pressure. Prior to polymerization, the styrene monomer was added drop wise to excess methanol to detect the presence of polymer in the monomer [29]. The initiator AIBN was recrystallised from methanol and vacuum dried.

3.2.2 Measurements

UV - Visible spectra were recorded on a Shimadzu UV - 160 spectrophotometer at room temperature. C, H, N analysis for monomers was carried out at Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow. ^{1}H NMR, ^{13}C NMR were obtained with Bruker 250 MHz and 20.1 MHz respectively with $CDCl_3$ as solvent and TMS as the internal standard. ^{31}P NMR spectra were recorded on a Bruker 101 MHz spectrometer. Phosphorus chemical shifts are reported with reference to external 85% H_3PO_4. The FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using argon as the FAB gas. The accelerating voltage was 10 Kv and the spectra were recorded at room temperature . Mass spectra were also recorded in EI mode. Powder X-ray diffraction patterns were obtained on a Rich-Seifort (Iso Debye Flex 200 2D) using Cu K $_{\alpha}$ radition at 30 Kv at room temperature. Gel permeation chromatography was carried out for a selected copolymer on a C - R4A Chromatopac using THF as a solvent. DSC and DTA studies were carried out on Perkin Elmer DSC-7 thermal analyser and Dupont 9900 thermal analyser respectively.

3.2.3 Synthesis of 4-Hydroxy-4'-Vinylbiphenyl (HVB)

3.2.3.1 Synthesis of 4-Acetoxy-4'-acetylbiphenyl (AAB)

To a stirred ice cold solution of anhydrous aluminium chloride (80.0g, 0.60mol) in dichloromethane ~~taken~~ in a three necked flask, freshly prepared acetyl chloride (40.1g, 0.51mol) was added dropwise. The mixture was stirred at 5°C for ~~half an~~ 0.5 hour. Solid 4-hydroxy biphenyl (40.0g, 0.24mol) was added slowly through the side neck. The solution turned pink ~~in colour~~. The reaction mixture was stirred continuously for 3 hours. The mixture was then poured into beaker containing crushed ice. The organic layer was separated and washed repeatedly with water. The organic layer was dried anhydrous sodium sulphate ~~and finally stripped off its~~ the solvent was removed *in vacuo* to afford a yellow solid which was recrystallized from methanol to give 4-acetoxy-4'-acetylbiphenyl

(AAB) (57.4g, 96%).

Melting point : 124°C.

^{1}H NMR (δ) 2.3 (s, 3H, $OCOCH_3$), 2.6 (s, 3H, $COCH_3$), 7.4, (m, 8H, phenyl).

3.2.3.2 Synthesis of 4-Hydroxy-4'-hydroxy ethyl biphenyl (HEB)

To a stirred solution of AAB (40.0g, 0.16mol) in methanol (500ml) sodium borohydride (6.0g, 0.16mol) in methanol (200ml), was added slowly through a dropping funnel. The mixture turned into a transparent yellow liquid. The mixture was stirred at room temperature for 6 hrs. From this solution most of the methanol was evaporated in vacuum to get a yellow oily liquid. 400ml of ethylacetate was added to the oily liquid and the solution was washed with 5% dilute hydrochloric acid. The ethyl acetate solution was washed with water and kept over anhydrous sodium sulphate. The solvent was stripped off in vacuum to obtain a pale yellow solid, which was recrystallized from ethylacetate. The solid was dried in vacuum at 50°C to get pure 4-hydroxy-4'-hydroxyethylbiphenyl (HEB) (32.7g, 97%).

Melting point : 145°C.

^{1}H NMR (δ) : 1.5 (d, H, CH_3), 4.9 (q, 1H, CH), 7.2 (m, 8H, phenyl)

3.2.3.3 Synthesis of 4-Hydroxy-4'-vinyl biphenyl (HVB)

In a two necked round bottomed flask (20.0g, 0.09mol) HEB was taken in 150ml dimethyl sulfoxide. To this solution anhydrous zinc chloride (4.0g, 0.09mol) was added at once. The mixture was stirred at room temperature for 30 minutes and then heated to 180°C for 20 minutes. Trichloro acetic acid (4.0g, 0.09mol) was added care-

fully through one neck of the flask. The mixture turns dark red in colour. The mixture was stirred for three minutes maintaining the temperature at 180°C. The mixture was brought to room temperature and poured into an excess of water to remove unreacted zinc chloride and trichloro acetic acid. Yellow solid precipitates from the oily liquid was filtered and dried in vacuum (8.9g, 49%).

Melting point : 192°C.

^{1}H NMR (δ) : 5.8 (dd, 3H, CH=CH_2), 7.4 (m, 8H, phenyl).

3.2.4 Synthesis of Hydroquinone mono acrylate (HQMA)

To an ice cold solution of thionyl chloride (34.3g, 0.77mol), acrylic acid (36.8g, 0.51mol) was added dropwise. The mixture was stirred at room temperature for 2 hrs. The resulting mixture was fractionated at 74°C to get a clear colourless liquid of acryloyl chloride (33.0ml, 80%). A freshly distilled sample of acryloyl chloride (6.1g, 0.07mol) in 100ml THF was added to a mixture of hydroquinone (7.5g, 0.07mol) and triethylamine (13.8g, 0.14mol) in 200 ml THF . After the addition the mixture was stirred at room temperature for 12 hrs and then refluxed at 60°C for 2 hours. The mixture was then brought to room temperature. Amine hydrochloride was separated by filtering through a sintered funnel. The solvent THF was removed at reduced pressure. The oily liquid was washed with water and kept over anhydrous sodium sulphate. The oily liquid was subjected to silicagel (100-200) silicagel column chromatography using 80% hexane and 20% ethyl acetate mixture. The initial fraction corresponds to the less polar di-substituted derivative. Pure hydroquinone mono acrylate (HQMA) was obtained as an oily liquid (4.3g, 39%) which solidifies when it was kept inside the ice chest for two months.

Melting point : 67°C.

Infrared(cm^{-1}) : 3380(m), 3320 (m), 1710(s), 1700(s), 1500(s), 820(s).

^{1} H NMR (δ) : 5.9 (dd, 1H, -CH=CH_2), 6.3 (dd, 1H, -CH=CH_2), 6.8 (m, 4H, phenyl)

3.2.5 Synthesis of 4-hydroxy styrene (PHS)

P-hydroxy benzaldehyde (61.0g, 0.5mol) was dissolved in 100ml freshly distilled pyridine. To this Malonic acid (52.0g, 0.5mol) was added and the reaction mixture was stirred thoroughly. To this homogeneous mixture aniline (2.5g, 0.03mol) was added. The mixture was stirred at room temperature for three weeks and then poured into a beaker containing hydrochloric acid and crushed ice, ~~mixture~~. The dark brown ~~solid~~ precipitate was washed with water. The solid was separated and dried in vacuum. Pure 4-hydroxy cinnamic acid was obtained by recrystallizing in a water-methanol (3:1) mixture (43.7g, 53%) Melting point: 210°C. 4-Hydroxy styrene was obtained by heating 4-hydroxy cinnamic acid (5.0g, 0.03mol) in a cold finger apparatus at 220°C at 0.01 mm Hg. Carbon dioxide was liberated and a white crystalline solid condensed on the cold finger. The solid was washed with dry benzene. The solvent was removed under pressure to afford a white solid (PHS) (1.3g, 36.6%.)

Melting point : 72°C.

^{1}H NMR (δ) : 5.5 (dd, 1H, CH=CH_2), 6.8 (dd, 1H, CH=CH_2), 7.4 (d, 4H, phenyl), 2.2 (s, 1H, OH).

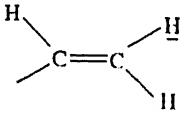
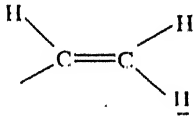
3.2.6 Synthesis of 2-(4'-vinyl-4-biphenylyloxy)-2,4,4,6,6,8,8-heptachlorocyclotetraphosphazene (TETHVB)

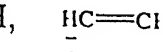
To a stirred solution of octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) (4.7g, 0.01mol) in benzene a mixture of 4-hydroxy-4'-vinylbiphenyl (HVB) (2.0g, 0.01mol) and triethylamine (1.0g, 0.01mol) in benzene was added dropwise. The mixture was stirred at room temperature for 12 hours. Amine hydrochloride was separated by filtration. The solvent was evaporated under reduced pressure to obtain an oily liquid. The oily liquid was subjected to silica gel column chromatography using hexane as an eluent. After the removal of unreacted $N_4P_4Cl_8$ in the first fraction TETHVB was obtained. Evaporation of hexane gave a white powder (1.6g, 26%).

Melting point : 104°C.

UVλ(max)($CHCl_3$) : 280.8 nm

Infrared (cm^{-1}) : 1490(s), 1300(vs), 1200(s), 1180(s),1020(s), 970(s), (900(s), 790(s).

^{1}H NMR (δ) : 5.3(dd, 1H, ), 5.8 (dd, 1H, )

6.75 (dd, 1H, ), 7.5 (m, 8H, phenyl).

^{13}C NMR (δ) : 128.54, 128.42, 127.39, 126.93, 121.67.

^{31}P NMR (δ) : 5.8 (m, 1P, PCl(OR)), 11.7 (t, 2P, PCl_2).

Mass ($C_{14}H_{11}ON_4P_4Cl_7$) : 623 ; found (M^+) = 623.

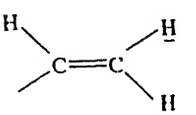
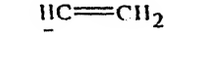
3.2.7 Synthesis of 2-(4-acryloyloxyphenoxy)heptachlorocyclo tetraphosphazene. (TETQMA)

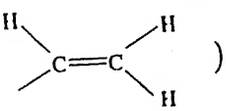
To a stirred solution of octachloracyclotetraphosphazene (2.8g, 6.0mmol) in 100ml benzene, a mixture of hydroquinone monoacrylate (HQMA) (1.0g, 6.0mmol) and triethylamine (0.6g, 6.0mmol) in benzene was added dropwise through a dropping funnel. The mixture was stirred at room temperature for 12 hours. Amine hydrochloride was separated by filtration. The solvent was removed under reduced pressure. A yellow oily liquid was obtained which was subjected to column chromatography. Unreacted $N_4P_4Cl_8$ was obtained in the first fraction when eluted with hexane. TETQMA was separated by using a mixture of hexane 90% ethylacetate 10% mixture as the eluent. The solvent was evaporated to get a yellow oily liquid which solidifies when it was kept inside the ice chest for two weeks. (1.7g, 47.7%).

Melting point : 45°C.

UV λ(max)($CHCl_3$) : 245.5 nm.

Infrared (cm^{-1}) : 1740 (s), 1490 (vs), 1300 (m), 1170(s), 960 (s), 1010(s), 890(s), 780(s).

^{1}H NMR (δ) : 6.0 (dd, 1H, ), 6.3 (dd, 1H, )

6.6 (dd, 1H, ), 7.5 (m, 4H, phenyl).

^{13}C NMR (δ) : 134.0, 127.8, 123.0, 123.0, 122.0.

^{31}P NMR (δ) : - 5.8 (m, 1P, PCl(OR)) , - 11.7 (t, 2P , PCl_2).

Mass ($C_9H_7N_4O_3P_4Cl_7$) : 591 ; found (M^+) = 591 .

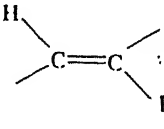
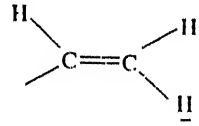
3.2.8 Synthesis of 2, (4-Vinylphenoxy)-2,4,4,6,6,8,8-heptachlorocyclotetraphosphazene (TETPHS)

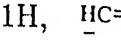
A mixture of 4-hydroxy styrene (0.6g, 5.0mmol) and triethylamine (0.5g, 0.005mol) in benzene was added dropwise to a stirred solution of octachlorocyclotetraphosphazene (2.3g, 5.0mmol) in 100ml benzene. The mixture was stirred at room temperature for 15 hours. Amine hydrochloride was separated by filtration. The solvent was stripped off *in vacuo*. The oily liquid obtained was subjected to silicagel column chromatography. Since this monomer was found to degrade in presence of light, the column was run in diffuse light.Initial fraction corresponds to unreacted $N_4P_4Cl_8$ when the column was eluted with hexane. TETPHS was obtained in the second fraction. The solvent was removed under reduced pressure to get a colourless oil which solidified when it was kept inside the ice chest for two days. (1.2g, 41.7%).

Melting point : 40°C.

UV λ(max) ($CHCl_3$) : 252.6 nm.

Infrared (cm^{-1}) : 1490 (s), 1300(vs), 1200(vs), 1190(vs), 1010(s), 970(s), 900(s), 770(s).

^{1}H NMR (δ) : 5.3 (dd, 1H,  , 5.6 (dd, 1H, ),

6.7 (dd, 1H, ), 7.3(m, 4H, phenyl).

^{13}C NMR (δ) : 127.8, 121.2, 114.9, 121.5.

^{31}P NMR (δ) : 5.7 (m, 1P, PCl(OR)), 11.5 (t, 2P, PCl_2).

Mass ($C_8H_7ON_4P_4Cl_7$) : 547 ; found (M-1) = 546.

3.3 Homopolymerization studies of TETHVB

TETHVB (1.0g, 1.0mmol) was taken in 20 ml s-tetrachloro ethane with AIBN initiator (53.0mg, 0.32mmol) in a thick glass ampoule. The ampoule was degassed thrice by freeze-thaw procedure. and sealed under vacuum. The polymerization was carried out for 14 hours at 70°C. The mixture obtained was poured into methanol to afford a white precipitate. The solid precipitated was redissolved in s-tetrachloroethane and then poured into fresh methanol. This process was ~~carried out~~ repeated for three times to give a material which was dried in vacuum at 50°C (0.6g, 63%).

^{1}H NMR (δ) : 2.0 (m, CH_2), 7.0 (m, phenyl).

^{31}P NMR (δ) : 3.0 (m, 1P , PCl(OR)), 11.7 (t, 2P, PCl_2).

The other polymerization experiments done for TETHVB under various conditions are summarized in Table 3.1.

Table 3.1: Homo Polymerization of TETHVB Under Various Conditions.

TETHVB Moles	AIBN Moles	Reaction time, hrs	Solvent used	Recovered monomer, g	Polymer Obtained %
9.4×10^{-4}	1.8×10^{-5}	48	1,2-DCE	0.49	-
6.2×10^{-4}	1.2×10^{-5}	72	-do-	0.36	-
7.9×10^{-3}	1.6×10^{-5}	15	Benzene	0.346	-
1.6×10^{-3}	3.2×10^{-5}	14	TCE	-	63

Table 3.2 summarizes the copolymerization of TETHVB with styrene.

why not in moles? for easy comparison.

Table 3.2

Copolymer code	TETHVB moles	STYRENE moles	Total moles	Feed ratio %
HVBSTY1	8×10^{-4}	8×10^{-4}	1.6×10^{-3}	28.6
HVBSTY2	8×10^{-4}	6×10^{-4}	1.4×10^{-3}	22.4
HVBSTY3	8×10^{-4}	4×10^{-4}	1.2×10^{-3}	17.6
HVBSTY4	8×10^{-4}	3×10^{-4}	1.1×10^{-3}	19.8
HVBSTY5	8×10^{-4}	1×10^{-4}	9.6×10^{-3}	12.6

3.4 Results and discussion

3.4.1 Synthesis of $N_4P_4Cl_7(C_{14}H_{11}O)$ (TETHVB), $N_4P_4Cl_7(C_9H_7O_3)$ (TETQMA) and $N_4P_4Cl_7(C_8H_7O)$ (TETPHS)

The precursors 4-hydroxy-4'-vinylbiphenyl (HVB) [24], hydroquinone monoacrylate (HQMA) [25] and 4-hydroxy styrene (PHS) [26,27] were synthesised by literature procedures. HVB is pale yellow in colour and it becomes dark yellow when exposed to light for a prolonged time. HQMA is a low melting solid; however it can be solidified by keeping inside an ice chest(0°C) for two months. PHS can be prepared by subliming 4-hydroxy cinnamic acid in a cold finger apparatus. PHS is also very sensitve to light and moisture. These difunctional reagents were reacted with octachlorocyclotetraphosphazene at room temperature in benzene or toluene for 12 hours with triethylamine as a hydrochloride scavenger (Figure 3.4). Invariably all the compounds had to be purified by column chromatography. However, the compounds degrade quickly in the silicagel columns particularly in presence of light as indicated by the formation of coloured bands in the column. In order to avoid this, the columns were run either in diffused light, or coverd with aluminium foil. The yields after purification were TETHVB (26%), TETQMA (47.7%), and TETPHS (41.7%). It is interesting to note that the analogous reaction with $N_3P_3Cl_6$ affords the mono substituted derivative in varying yields CPHVB (45%), TQMA (50.4%), VPCP (48%). These later derivatives however, are much more stable towards hydrolysis in comparison with the cyclotetraphosphazene derivatives TETHVB, TETQMA and TETPHS.

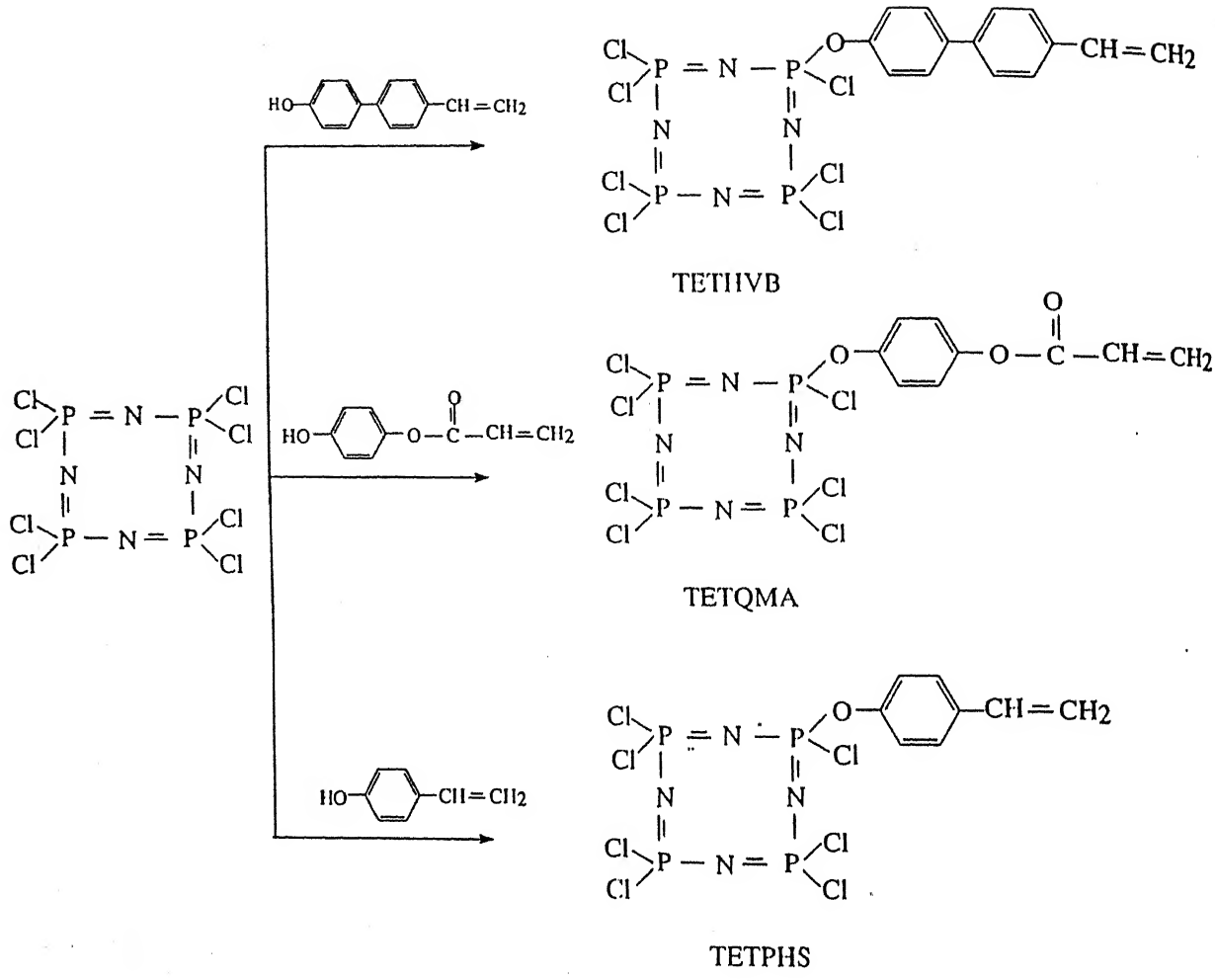


Figure 3.4 Synthetic Route Involved the Preparation of TETHVB, TETQMA and TETPHS.

3.5 Structural Characterization of TETHVB, TETQMA and TETPHS

The mass spectra of the cyclotetraphosphazene derivatives were recorded both under electron impact and FAB mass spectral conditions. In both of these methods the parent ion peak is predominantly seen at 624, 591 and 546 respectively. An interesting feature of the mass spectra is that while in TETQMA the first major fragmentation is by the loss of the $-COCH = CH_2$ group with almost no initial chlorine fragmentation, in the case of TETHVB and TETPHS although the initial fragmentation is due to the loss of the vinyl group there is a simultaneous two-chlorine loss. In all cases the $N_4P_4Cl_7$ fragment is quite predominant; this undergoes subsequent stepwise chlorine loss. Some representative FAB mass and EI mass spectra are shown in Figure 3.5 and 3.6 respectively.

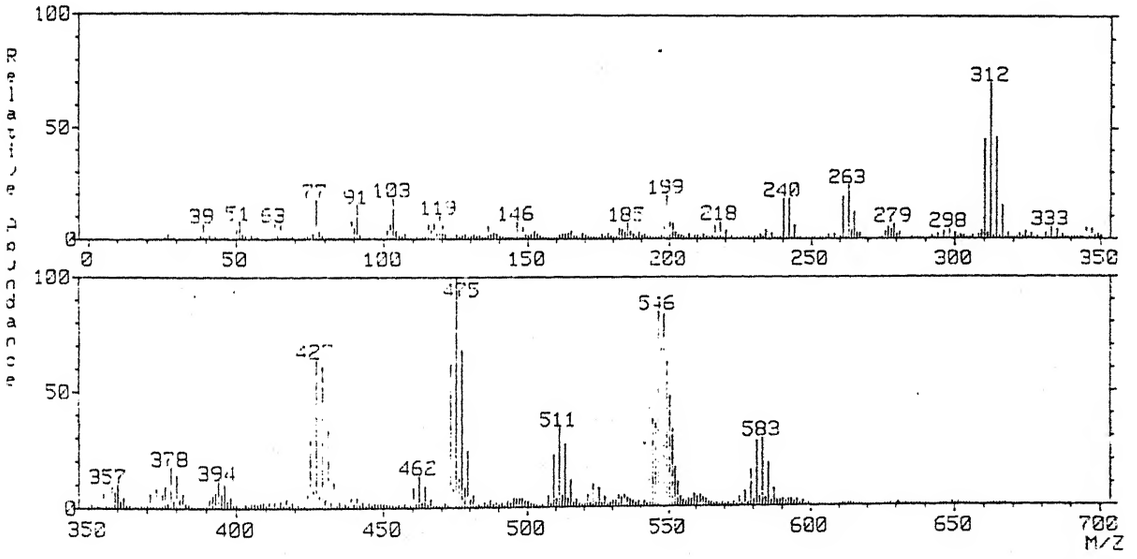


Figure 3.5: FAB Mass Spectrum of TETPHS.

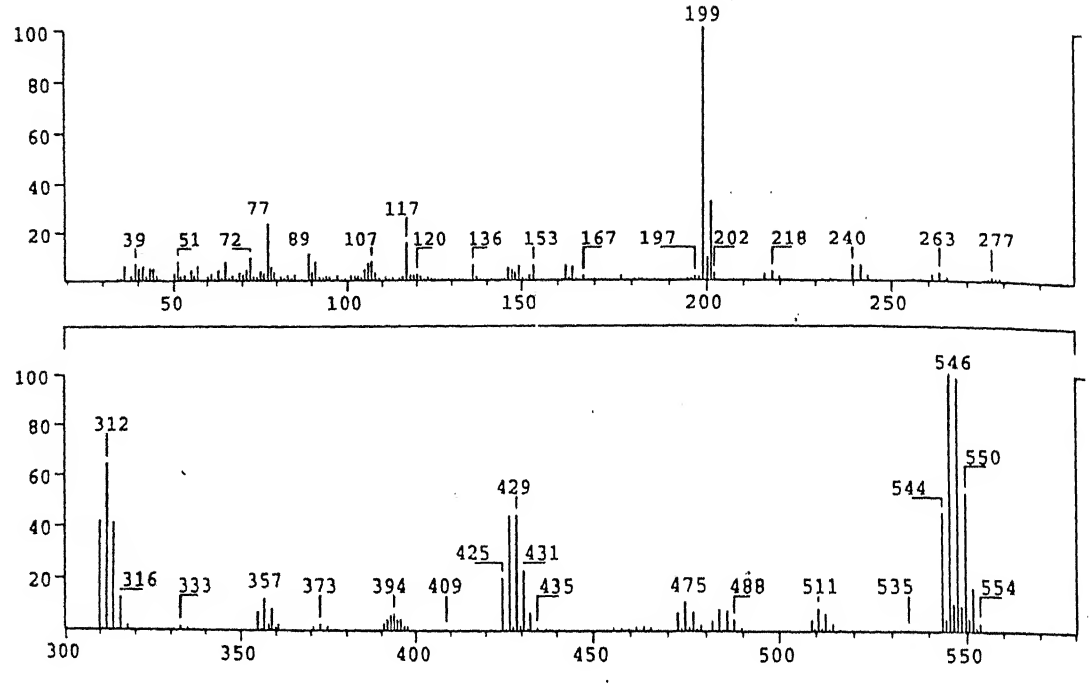


Figure 3.6: EI Mass Spectrum of TETPHS.

The proton NMR spectra of TETHVB, TETQMA and TETPHS show that the vinylic region is either of an ABX (TETQMA) or an (AMX) type (TETHVB, TETPHS). Representative ^{1}H NMR spectra are shown in Figure 3.7. As expected the protons for the 'X' region are considerably deshielded and are seen around 6.8 -6.9 ppm. Table 3.3 summarizes this data.

Table 3.3. ^{1}H NMR Data for TETHVB, TETQMA and TETPHS.

Compounds	δ Ph	δ A	δ B	δ X	J_{A-B}	J_{A-X}	J_{M-X}
TETHVB	7.40	5.81	5.30	6.75	17.6	10.9	0.82
TETQMA	7.23	6.60	6.00	6.30	17.2	10.3	1.43
TETPHS	7.30	5.70	5.27	6.7	17.59	10.88	-[a]

[a] Complex spectrum could not be assigned.

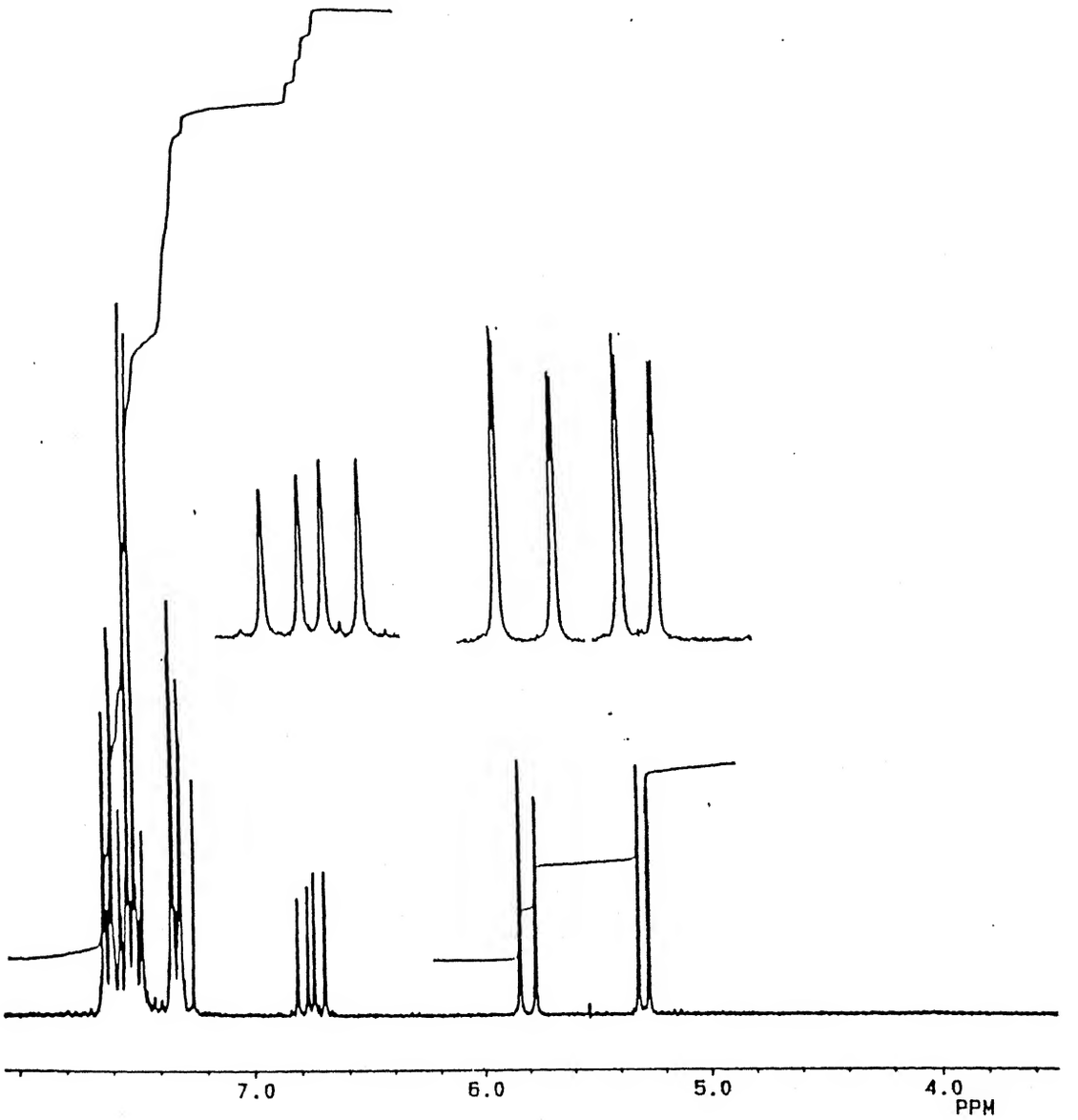


Figure 3.7 ^{1}H NMR Spectrum of TETHVB.

As expected $J_{(A-M)}$ and $J_{(A-X)}$ values are much larger than $J_{(M-X)}$. Thus the $J_{(A-M)}$ portion appear only as two doublets, where as doublets of doublets were expected. In all cases the chemical shifts of the A and M protons are considerably upfield shifted with respect to the X region. The aromatic resonances in the case of TETQMA and TETPHS and TETHVB are quite complex and deshielded with respect to all other protons. The ^{31}P NMR spectra of TETHVB, TETQMA and TETPHS are quite complex (Figure 3.8) as a result of the four spin system. They typically show an AB_2X pattern, with the X region (PClR) being more upfield shifted compared to (PCl_2). Comparison of chemical shifts obtained in the present instance with that of the literature chemical shifts known for the cyclophosphazene derivatives (Table 3.4) clearly shows that all the related derivatives appear down field. These trends are in accord with phosphorus chemical shifts trends known in cyclophosphazene literature.

Table 3.4: ^{31}P NMR Data for Various Cyclotriphosphazene Monomers.

Monomers	δ PRR'	δ PCl_2	Ref.
$N_3P_3Cl_5(OCH=CH_2)$	13.2	23.4	30,31
$N_3P_3Cl_5(OC(CH_3)=CH_2)$	10.2	22.3	32
$N_3P_3Cl_5(OC(C_6H_5)=CH_2)$	12.4	23.0	32
$N_3P_3Cl_4(CH_3)(OCH=CH_2)$	29.6	21.6	32
$N_3P_3Cl_4(CH_3)OC(CH_3)=CH_2)$	30.0	21.2	32
$N_3P_3Cl_4(CH_3)OC(C_6H_5)=CH_2)$	32.8	23.4	32

Thus mass, and multinuclear NMR spectra unambiguously prove the structures of TETHVB, TETQMA and TETPHS as mono substituted cyclotetraphosphazene derivatives.

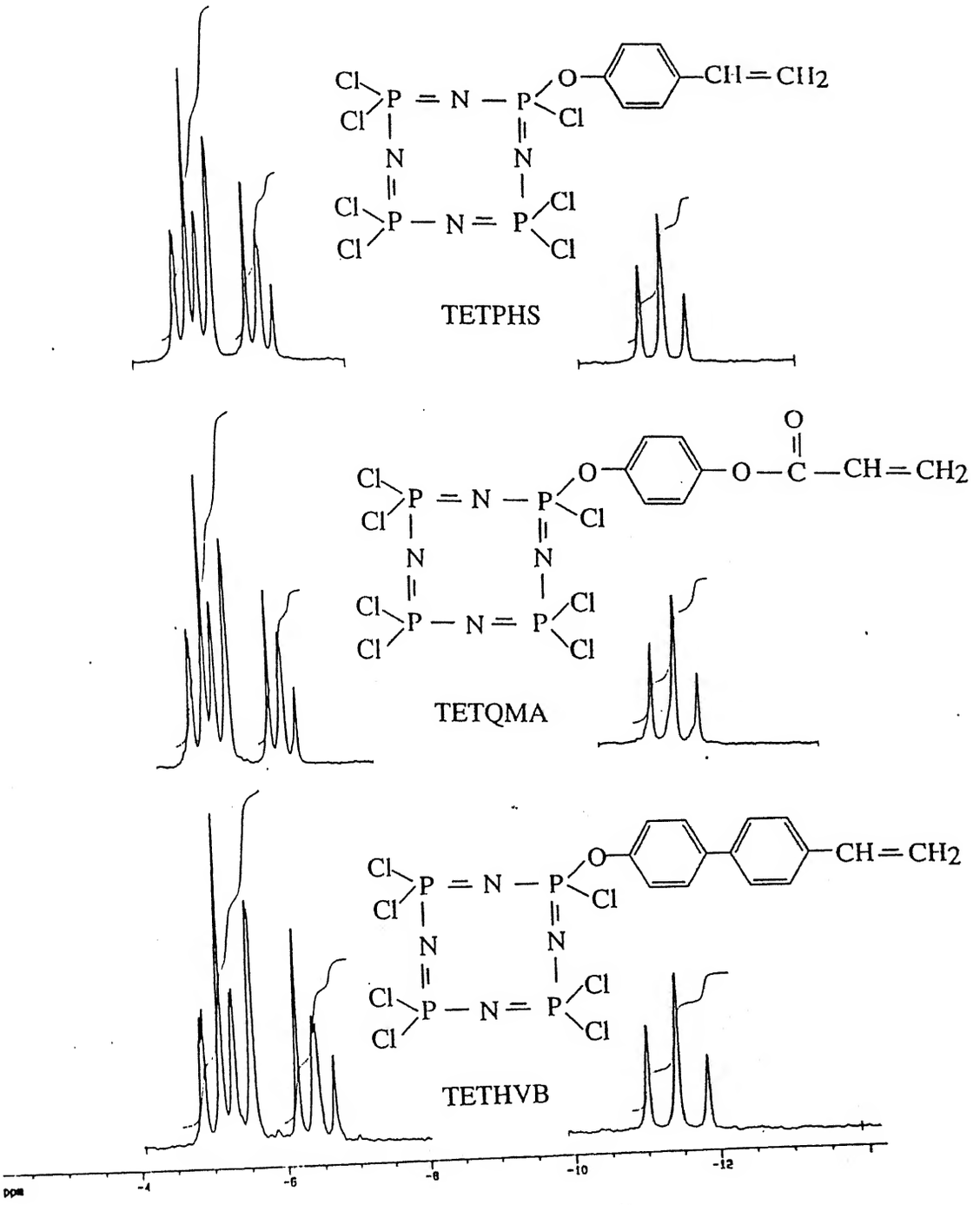


Figure 3.8: ^{31}P NMR Spectra of TETHVB, TETQMA and TETPHS.

3.6 Polymerization behaviour of TETHVB, TET QMA and TETPHS

Attempted homopolymerization of these cyclotetraphosphazene monomers by free radical methods in benzene or 1, 2 -dichloromethane for prolonged periods of time resulted in almost no polymerization (Table 3.1). This was confirmed by analysing the recovered material by ^{1}H NMR. Polymerization were attempted under sealed tube conditions (having sealed tubes containing reactants after repeated freeze thaw cycles) as well as under nitrogen. However, when the reaction medium was changed to symmetrical tetrachloro ethane TETHVB was found to under go homopolymerization (*see experimental* 3.4). The homopolymerization of TETHVB yielded 63% polymer (TETPOL 1). The polymer is a free flowing white powder, which tends to degrade upon exposure. This is presumably due to the reactivity of P-Cl bonds with moisture leading to crosslinked products as well as hydrolysis. It is interesting to compare the stability of the analogous homopolymer obtained from $N_3P_3Cl_5(C_{14}H_{11}O)$ which is very stable to atmosphere. This dramatic difference in behaviour can be accounted for as due to the enhanced reactivity of P-Cl bonds in cyclotetraphosphazene ring in comparison with cyclotriphosphazene ring. This difference in reactivity has been illustrated in many well studied examples It was not possible to study the homo polymerization of TETQMA and TETPHS in tetrachloroethane because of poor shelf lives of these monomers.

The proton NMR spectrum of TETPOL 1 shows the complete absence of vinylic protons which were seen as ABX pattern for the monomer. Also the ^{31}P NMR of TETPOL 1 suggest the essential retention of cyclophosphazene ring in the polymer. This is indicated by the near nonvariance of the ^{31}P chemical shifts. Similar observation was made by Selvaraj and coworkers in their investigation on $N_3P_3Cl_5(C_{14}H_{11}O)$. The DSC analysis of the homo polymer indicates a glass transition around 200°C and two decomposition around 344.5°C and 587.4°C respectively. The powder X-ray diffraction of the homopolymer indicates that it is an amorphous material.

Inorder to find out whether TETHVB can be copolymerized we tried copolymerization with styrene. The experimental details are summarized in Table 3.2. All of these polymers also show the retention of cyclotetraphosphazene ring as indicated by its ^{31}P NMR. Gel permeation chromatograph study showed that molecular weight of the styrene copolymer (HVBSTY 1) is 1 x 10^5 (Mw) with the polydispersity of 1.96. The glass transitions of the copolymers are lower than that of the homopolymer besides showing complete decomposition at 640°C. Table 3.5 summarizes glass transition temperatures of the homo and copolymers.

Table 3.5 Glass Transition Temperatures of the Homo and Copolymers of TETHVB.

Polymer	T_g °C	Ref.
TETPOL1	190	Present work
HVBSTY1	231	- do -
HVBSTY2	235	- do -
HVBSTY3	196	- do -
HVBSTY4	200	- do -

The thermal stability and degradation behaviour of TETPOL 1 was investigated in nitrogen. The decomposition of TETPOL 1 in nitrogen starts at 205°C. The major fragmentation occurs at 440°C. The most important feature of this polymer is its high char yield, i.e., char yield is 35.7% in nitrogen at 850°C (Figure 3.9). Thus TETPOL 1 has a potential use as heat and fire resistant polymer. Flame resistant property was also confirmed by simple flame tests. Thus these polymers were found to self extinguish when they were burnt in air.

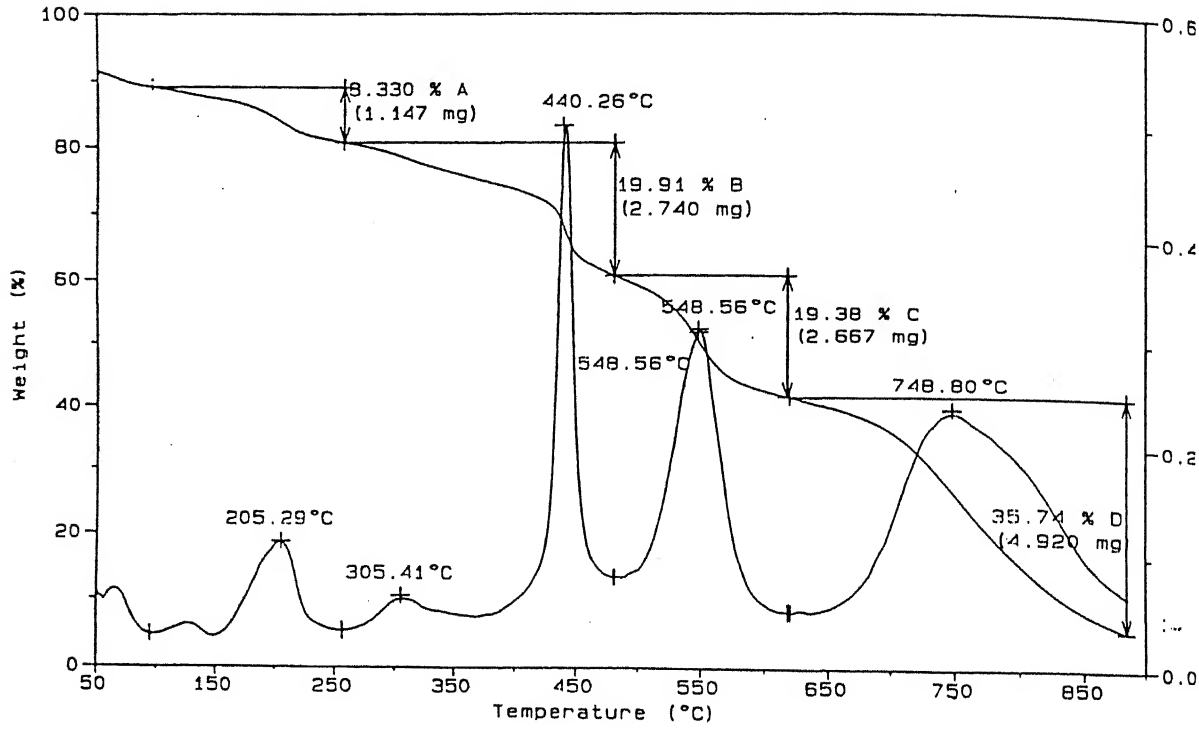


Figure 3.9. TGA Thermogram of TETPOL 1.

3.7 Conclusions

The result obtained in this chapter can be summarized as follows.

1. $N_4P_4Cl_8$ reacts with HVB, HQMA or PHS in presence of triethylamine to afford monosubstituted derivatives $N_4P_4Cl_7(C_{14}H_{11}O)$ (TETHVB), $N_4P_4Cl_7(C_9H_7O_3)$ (TETQMA), and $N_4P_4Cl_7(C_8H_7O)$ (TETPHS).

2. These monomers are extremely sensitive to hydrolysis. It has been found that of these three monomers TETHVB has a better stability and can be homopolymerized to afford a high molecular weight polymer. DSC and DTA studies carried out for these polymers suggest a high glass transition temperature.

3. TETHVB can also be incorporated into copolymers as indicated by copolymerization studies with styrene.

4. In sharp contrast to the polymers obtained from $N_3P_3Cl_5(C_{11}H_{14}O)$, polymers obtained from tetrameric systems are much less stable to ambient moisture causing hydrolysis and crosslinking.

5. The homo and copolymers possess flame resistant properties as shown by simple flame tests.

3.8 References

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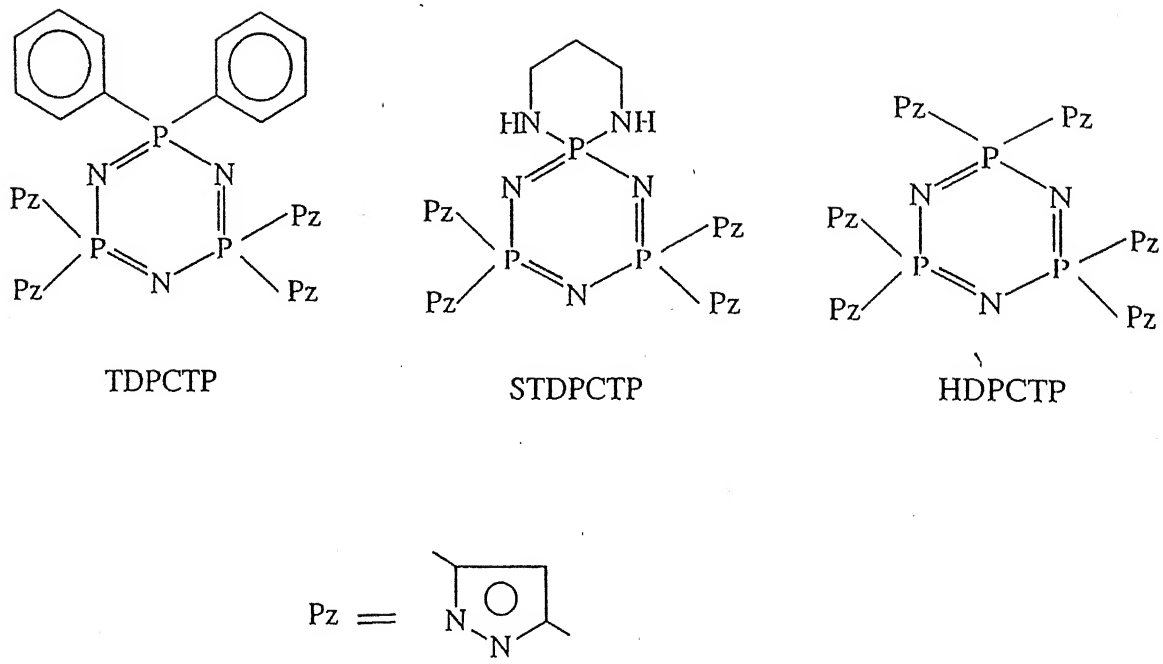


Figure 4.1: Structures of Selected Pyrazolyl Phosphazene Ligands.

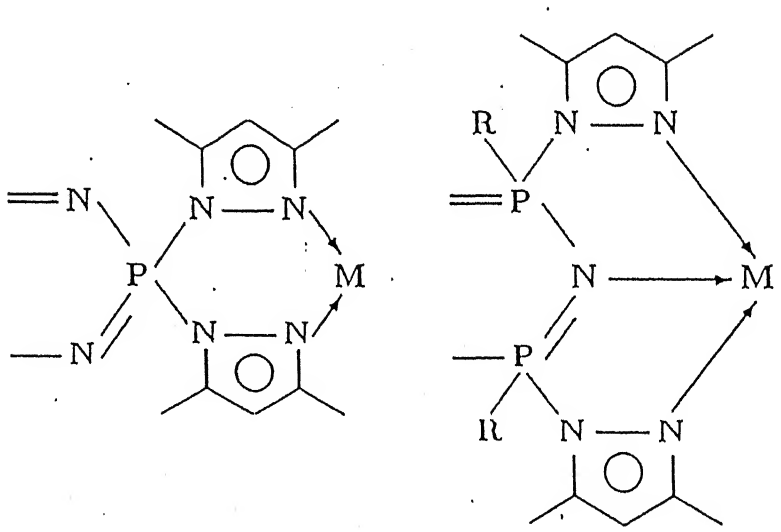


Figure 4.2: Different Coordination Modes of Pyrazolylphosphazenes.

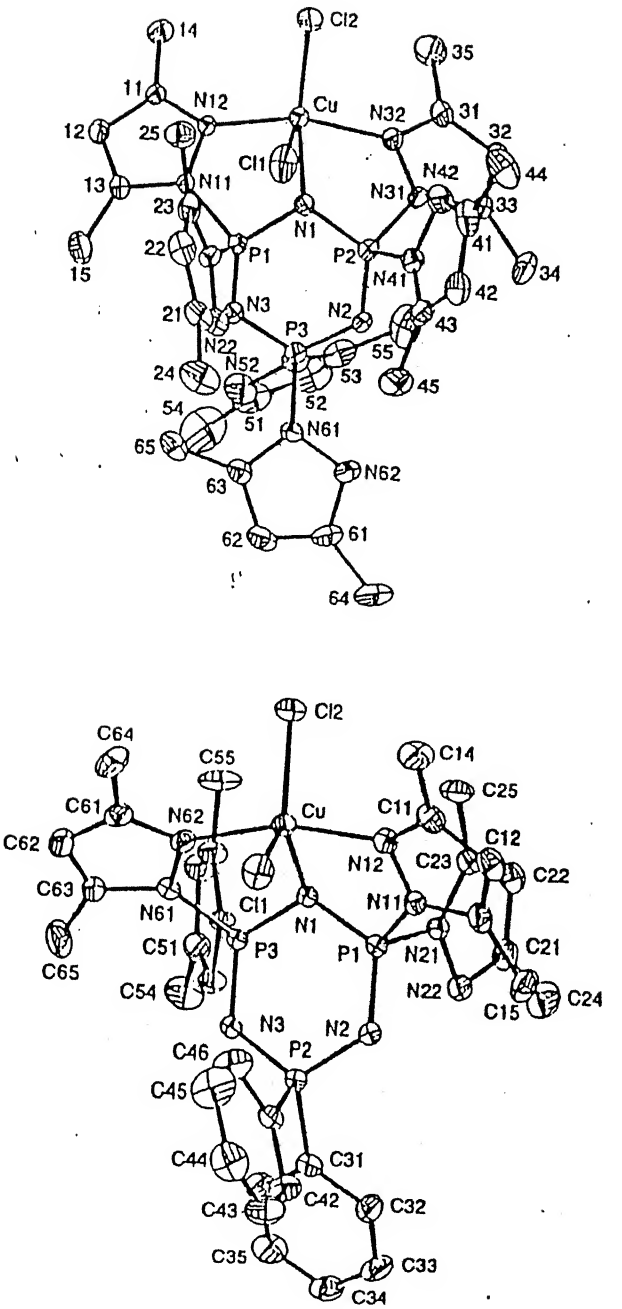


Figure 4.3: Crystal Structures of HDPCTP.$CuCl_2$.CH_2Cl_2 and TDPCTP.$CuCl_2$.

Also heterobimetallic derivatives were accessible from these multisite coordination system. An interesting aspect of the Pd, Cu heterobimetallic compound is the varying coordination pattern shown by the ligand [3]. Thus palladium is bound exclusively by the geminal pyrazoles, where as copper is linked through two nongeminal pyrazolyl nitrogens and one cyclophosphazene ring nitrogen.

4.2 Phosphazene Polymers Containing Heterocyclic Pendant Groups

In contrast to simple cyclophosphazenes which have been studied as coordination ligands, there are very limited examples of studies involving phosphazene polymers as ligands towards coordination to metals [4-6]. We have reasoned that novel coordinating polymers based on P-N motiffs are accessible in two ways.

1. By substituting the chlorine atoms in polydichlorophosphazene with suitable coordinating groups.

2. By incorporating a multi site coordinating cyclophosphazene ligand in the backbone of an organic polymer.

This chapter discusses both these approaches. In view of our experience with pyrazolylcyclophosphazenes we have used the pyrazole group in both the approaches.

In his pioneering study Allcock and coworkers investigated polyorganophosphazenes containing heterocyclic side groups such as furan, thiophene and pyrrole derivatives [4]. These novel polyphosphazenes were prepared by the reaction of polydichlorophosphazene with the sodium salt of the corresponding heterocyclic alkoxide. The prepared

polyphosphazenes were doped with $Fe(ClO_4)_2$, $FeCl_3$ or I_2 to give semiconducting polymers.

Allcock and coworkers have also synthesized a novel phosphazene polymer containing imidazolyl substituents [7,8] (*see Figure 4.4*) as they are very useful bio-erodible materials. These polymers were found to be highly unstable and they decompose in moist air to afford imidazole, phosphoric acid and ammonia. Introduction of a hydrophobic co-substituent group such as aryloxy reduces the rate of erosion. Allcock and coworkers have also studied poly[bis(methylamino)phosphazene and prepared its Pt(II) derivative [5]. This polymer was shown to posses antitumour activities.

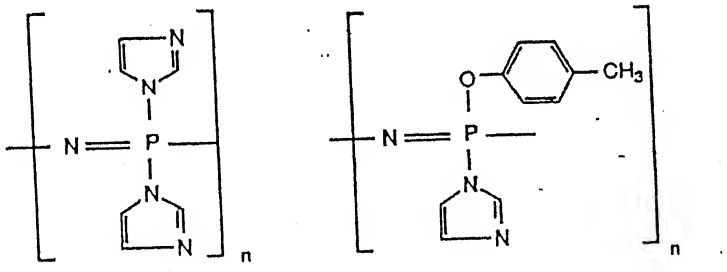


Figure 4.4: Examples of Imidazolyl Phosphazene Polymers.

The above discussion emphasizes the need for the development of phosphazene polymers having coordinating groups that are stable at room temperature, and that are also robust and relatively stable to hydrolysis.

In the first approach poly[bis(3,5-dimethylpyrazolyl)phosphazene] was prepared by the substitution of chlorines on polydichlorophosphazene with 3,5-dimethyl pyrazole. In order to understand the nature of this polymeric ligating system an x-ray structure of the simple model compound $N_3P_3Pz_6$ was carried out. Further, as model studies, a trimeric ligand $N_3P_3(NH_2)_2Pz_4$ (DIAMPZ) and a tetrameric ligand $N_4P_4Pz_8$ (TETPZ) were also prepared and their coordination complexes particularly with Cu(II) and Co(II) were studied. Thus an x-ray structure of DIAMPZ.$CoCl_2$ was carried out. Interaction of $N_4P_4Pz_8$ with $CuCl_2$ affords a bimetallic derivative that is partially hydrolyzed. This lability of pyrazolyl groups in the eight membered cyclotetraphosphazene ring is to be contrasted with the earlier studied six membered ring. Attempts to isolate a $CoCl_2$ derivative with TETPZ aslo resulted in complete decomposition. The isolated crystals were shown to be $CoCl_2Pz_2$. The polymeric derivatives POLYM 1 and CAPYP was interacted with copper chloride to isolate relatively stable complexes. Spectroscopic studies on this complex suggest five coordinate geometry around copper. However from spectroscopic studies it is not possible to unambiguously arrive at the structure of the complex. Clearly pyrazolyl to copper coordination must be present; however, the interaction of the skeletal nitrogen atoms belonging to the polyphosphazene backbone with copper cannot be ascertained with the available data.

The pendant cyclophosphazene containing polymer was prepared by reacting 4-hydroxy-4'-vinylbiphenyl (HVB) with $N_3P_3Cl_6$ and then, the mono substituted derivative $N_3P_3Cl_5$ O HVB (CPHVB) was reacted further with 3,5-dimethylpyrazole to obtain $N_3P_3Pz_5$ O HVB (PPHVB) which contains a polymerizable functionality. Polymerization of PPHVB has been carried out by using free radical methods to obtain a polymer (POLYM 1) containing PPHVB unit. Both PPHVB and the POLYM 1 have

been shown to interact with $CuCl_2$ and $CuBr_2$. The coordination mode is inferred as being similar to what was observed earlier with $N_3P_3Pz_6$ and $N_3P_3Ph_2Pz_4$.

4.3 Experimental

4.3.1 Materials

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ and octachlorocyclotetraposphazene, $N_4P_4Cl_8$ (Nippon Soda, Japan) were recrystallized from petroleum ether and n-pentane to constant melting (114°C, 123°C) solids prior to use. 3,5-Dimethyl pyrazole [9] was prepared by adapting the published methods. CPHVB was synthesized by literature procedure [10]. The initiator AIBN was recrystallized from methanol and vacuum dried before use. Polydichlorophosphazene was synthesized by melt polymerization of hexachlorocyclotriphosphazene [11]. Commercially precured hydrated coppper halides and cobalt chloride were dried by heating at their dehydration temperatures in a oven for atleast 10hrs and stored in a desiccator over dry $CaCl_2$.

4.3.2 Measurements

Metal contents were determined complexometrically by indirect titration with Na_2H_2 EDTA after destruction of the sample with con.HNO_3 acid [12]. C, H and N analyses were performed at the micro analytical centre, RSIC, CDRI, Lucknow. Infrared spectra were recorded on a Perkin-Elmer1320 spectrophotometer. Samples were prepared as potassium bromide pellets or as nujol mulls. Electronic spectra were obtained with a Shimadzu UV-160 spectrophotometer. The EPR spectra were obtained on a Varian spectrometer. The magnetic field strength was calibrated with dpph (g=2.003). The ^{1}H NMR spectra were obtained on a Bruker spectrometer operating at 80 or 400MHz, and chemical shifts are reported with reference to internal tetramethyl silane. Phosphorus 31 NMR spectra were recorded on a Bruker MY043 RY spectrometer operating at 161.9 MHz. Phosphorus chemical shifts are reported with reference to external 85% H_3PO_4. Upfield shifts are negative. The FAB mass spectra were recorded on a JEOL

SX 102/DA-6000 mass spectrometer using argon (6kV,10mA) as the FAB gas. The accelerating voltage was 10kV and the spectra were recorded at room temperature. m-Nitrobenzyl alcohol was used as the matrix. Solution magnetic susceptibilities of the complexes were measured at 27°C by the Evans [13] NMR method which correlates the paramagnetic shift Δf to the volume magnetic susceptibility by:

$$\chi_v = \frac{3\Delta f}{2\pi f m} + \chi_o + \frac{\chi_o (d_o - d_s)}{m}$$

The last term is generally neglected as it is very small [14]. The molar magnetic susceptibility (χ_m) is related to the experimental temperature (T) and effective magnetic moment (μ_{eff}) as below:

$$\chi_m = \chi_v \times M.Wt$$

$$\mu_{eff} = 2.84 \sqrt{\chi_m T}$$

Thermal analysis (TGA, DTA and DSC) were done on a General V4.1c Dupont 2100, General V4.1c Dupont 2000 and Shimadzu DTA-50 thermal analyzers, respectively. Dilute solution viscosity measurements were carried out on a Schott-Gerate viscometer in THF at 30°C using an Ubbholde viscometer. Powder x-ray patterns of polymer samples were recorded on a Rich Seifort (Iso Debyeflex 200 2D) counter diffractometer using Cu K_α radiation operating at 30kV. All powder x-ray studies were done at room temperature. The data collection for the single crystals were carried out on a Enraf-Nonius CAD-4 diffractometer with a monochromatic Mo K_α radiation. Crystals were glued on glass fibers and transferred to a diffractometer. The data were collected at 25°C using θ-2θ scan technique.

4.4 Synthesis of Pyrazolylcyclophosphazenes

4.4.1 Hexakis(3,5-dimethyl-1-pyrazolyl)cyclotriphos phazene,$N_3P_3Pz_6$ (HDPCTP)

To a stirred solution of Hexachlorocyclotriphosphazene (3.0g, 8.0mmol) in benzene, a mixture of 3,5-dimethylpyrazole (5.8g, 0.06mol) and triethyl amine (6.1g, 0.06mol) was added dropwise. The mixture was stirred at room temperature for 30 minutes and then refluxed at 80°C for 6 hrs. The mixture was brought to room temperature. Precipitated amine hydrochloride was separated by filtration. The benzene solution was washed with water and kept over anhydrous sodium sulphate. The clear solution was filtered and the solvent was evaporated under reduced pressure to afford a white solid (5.7g, 94%), which was recrystallized from a 1:1 mixture of dichloromethane and hexane.

Melting point : 255°C

Infrared (cm^{-1}) : 2950(s), 1574(vs), 1450(s), 1410(s), 1220(vs),1170(vs), 966(s),756(s)

^{1}H NMR (δ) : 2.22 (s, 18H, 3-CH_3), 2.3 (s, 18H, 5-CH_3), 5.5(s, 6H, 4-CH)

^{31}P NMR (δ) : - 3.4 (s, $P(Pz)_2$)

4.4.2 2,2-Diamido-4,4,6,6-(3,5-dimethyl-1-pyrazolyl)cyclotri phosphazene $N_3P_3(NH_2)_2(Pz)_4$, (DIAMPZ)

4.4.2.1 2,2-Diamido,4,4,6,6-terachlorocyclotriphosphazene ($N_3P_3(NH_2)_2Cl_4$) (DACP)

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (3.5g, 0.01mol) was dissolved in 100 ml diethyl ether. Anhydrous sodium sulphate (10g) was added. To this heterogeneous mixture, a 25% ammonia ~~in water~~ (0.7g, 0.04mol) was added dropwise. The reaction mixture was stirred at 0°C for 8hrs. The reaction mixture was filtered. The solvent was removed ~~from the filtrate~~ under reduced pressure to obtain a white solid (2.4g,77%). Since DACP is highly sensitive to moisture it was used for subsequent reaction immediately.

4.4.2.2 2,2-Diamido-4,4,6,6-(3,5-dimethyl-1-pyrazolyl)cyclotri phosphazene $N_3P_3(NH_2)_2(Pz)_4$, (DIAMPZ)

To a strirred solution of DACP (2.4g, 7.0mmol) in 100ml benzene, a mixture of 3,5-dimethyl pyrazole (2.9g,0.03mol) and triethylamine (3.2g, 0.03mol) in 100ml benzene was added drop wise. Amine hydrochloride precipitated as soon as the addition started. The reaction mixture ~~was subjected to~~ reflux ~~conditions~~ (80°C) for 48 hrs. The mixture was brought to room temperature. The solvent was removed under reduced pressure to obtain a white solid (3.8g, 89%) which can be recrystallized from a 1:1 mixture of dichloromethane and hexane.

Melting point : 196°C

Infrared(cm^{-1}) : 3400(m), 3320(m), 3220(m), 2940(br), 2860(s), 1560(s), 1460(s), 1410(s), 1290(s), 1200(br), 1020(s), 960(s), 840(s), 790(s), 760(s).

^{1}H NMR (δ) : 2.0 (s, 12H, 3-CH_3), 2.1 (s, 12H, 5-CH_3), 3.3(br.s, 4H, NH),

5.8 (s, 4H, 4-CH)

^{31}P NMR (δ) : 1.5 (d, 2P, $P(Pz)_2$), 18.2 (t, 1P, $P(NH_2)_2$)

FAB Mass ($C_{20}H_{32}N_{13}P_3$) Calcd = 548 ; found =548 (M^+)

4.4.3 Octakis(3,5-dimethyl-1-pyrazolyl)cyclotetraphosphazene, $N_4P_4(Pz)_8$ (TETPZ)

To a benzene solution of octachlorocyclotetraphosphazene (1.0g, 2.0mmol), a mixture of 3,5-dimethylpyrazole (1.9g, 0.02mol) and triethyl amine (2.0g, 0.02mol) was added dropwise. The reaction mixture was stirred at room temperature for 6 hrs, and then refluxed at 80°C for 14hrs. The reaction mixture was then cooled. Amine hydrochloride salts were separated by filtration. The solvent was stripped off under reduced pressure. (since derivatives of cyclotetraphosphazenes were found to degrade in presence of moisture, its contact with water was rigorously avoided) The concentrated liquid was precipitated by pouring in to large excess (200 ml) hexane to afford a white powder (2.6g, 64%).

Melting Point : 220°C

Infrared (cm^{-1}) : 1560(s), 1400(m), 1300(br), 1270(br), 1170(m), 1150(m) 1100(s),

1030(s), 970(s), 770(s)

^{1}H NMR (δ) : 2.0 (s, 24H, 3-CH_3), 2.1(s, 24H, 5-CH_3) 5.6(s, 8H, 4-CH)

^{31}P NMR (δ): 5.4 (s, 4P, $P(Pz)_2$)

FAB Mass ($C_{40}H_{56}N_{20}P_4$): Calcd 940; found 939 (M-1)

4.4.4 2-(4'-Vinyl-4-biphenylyloxy)-2,4,4,6,6-pentachloro cyclotriphosphazene (CPHVB)

To a stirred solution of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, (6.2g, 0.02mol) in 100 ml of dry benzene, a solution of HVB (3.6g, 0.02mol) and triethy lamine (2.5ml, 0.02mol) , was added dropwise over a period of 30 minutes at room temperature. The resulting solution was stirred for an additional 6 hours. The amine hydrochloride formed in the reaction was removed by filtration. The solvent benzene was stripped off from the filtrate under reduced pressure to give an oily liquid. The oil was subjected to silica gel (60-120 mesh) using hexane as the eluant. After collecting the unreacted $N_3P_3Cl_6$ as the first fraction, the product CPHVB was collected and recrystallized from hexane to give pure CPHVB (3.1g, 58%)

Melting point : 112°C

Infrared (cm^{-1}) : 1600.1(m), 1521.5(m), 1492.0(s), 618.6(s), 590.8(vs)

^{1}H NMR ($CDCl_3$) : 5.3 (dd, $=CH_2$), 5.8 (dd, $=CH_2$), 6.9 (dd, -CH =)

7.4 (m, aromatic)

^{31}P NMR ($CDCl_3$) : 20.8 (d,P(OR)Cl) ; 10.6 (t,PCl_2)

Mass (EI) : Calcd = 507 ; found = 507 (M^+)

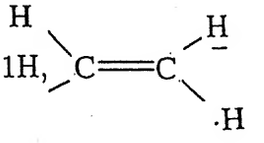
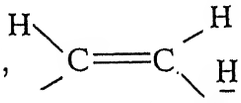
4.4.5 2-(4'-Vinyl-4-biphenylyloxy)-2,4,4,6,6-pentakis-(3,5-dimethyl-1- pyrazolyl)cyclotriphosphazene (PPHVB)

To a benzene solution of 2-(4'-vinyl-4-biphenylyloxy-2,4,4,6,6 - pentachlorocyclotriphosphazene (CPHVB) (3.0g, 6.0mmol) in a 250ml round-bottomed flask, a benzene solution of 3,5-dimethylpyrazole (3.4g, 0.04mol) and triethylamine (3.6g, 0.04mol) was added dropwise. The mixture was stirred at room temperature for 30 minutes and then refluxed at 80°C for 6 hrs.After allowing it to come to room temperature it was filtered. Solvent removal from the filtrate under reduced pressure. The oily liquid obtained was subjected to silica gel column chromatography. The title compound PPHVB was separated by using 25% ethyl acetate/ 75% benzene as the eluent. PPHVB was isolated as a pale yellow crystalline solid (2.7g, 45%).

Melting point : 146°C.

UV λ(Max) : 283.6nm

Infrared (cm^{-1}) : 1251(s), 1218(m), 1197(br), 1169(s), 964(m), 602(s).

^{1}H NMR (δ) : 2.1 (m, 30H, CH_3), 5.3 (dd, 1H, 
)
5.8 (dd, 1H, 
),
6.7 (dd, 6H, CH), 7.4 (m, 8H, Ph).

^{13}C NMR (δ) : 110, 127, 128, 137, 147.

^{31}P NMR (δ) : 3.1 (t, 1P, P(OR)), 0.4 (d, 2P, $P(Pz)_2$)

FAB Mass ($C_{39}H_{48}N_{13}OP_3$) Calcd : 806 ; found : 806 (M^+)

4.5 Synthesis of Pyrazolyl Phosphazene Polymers

4.5.1 Homopolymerization of 2-(4'-vinyl-4-biphenylyloxy)-2,4, 4,6,6 - pentakis -(3,5-dimethyl-1-pyrazolyl)cyclotriphos phazene

PPHVB was homopolymerized by dissolving (2.0g, 3.0mmol) of PPHVB in 20ml 1,2-dichloro ethane along with AIBN (8.1mg) as an initiator. The mixture was transferred into a thick glass walled ampoule. Then the tube was degassed by freeze-thaw procedure for three times and sealed. The tube was kept in an oil bath maintained at 70°C for 19 hrs. The tube was then cooled and opened. The contents were poured into a beaker containing excess (400ml) hexane. Reprecipitation was carried out for three times. The polymer precipitated was separated by filtration. The white solid obtained was vacuum dried and kept in the desiccator (1.7g, 87%).

Infrared (cm^{-1}) :3419(br), 2926(m), 1570(m), 1500(s), 1410(m), 1300(m), 1218(vs), 966(s), 824(m), 577(m).

^{1}H NMR (δ) : 2.4 (m, 33H, CH_3,CH_2), 5.8(s,5H, CH), 7.3(m, 8H, Ph)

^{31}P NMR (δ) : 2.7 (t, 1P, P(OR)), 0.1 (d, 2P, $P(Pz)_2$)

4.5.2 Poly[bis(3,5-dimethyl-1-pyrazolyl)phosphazene] (CAPYP)

Polydichlorophosphazene was synthesized by methods described in chapter 2 of this thesis *see experimental 2.5.1* . To a stirred solution of polydichlorophosphazene (2.0g, 0.01mmol) in 200ml THF, a mixture of 3,5-dimethylpyrazole (3.3g, 0.03mol) and triethyl amine (3.5g, 0.03mol) was added dropwise for 30 minutes. The mixture was stirred at room temperature for 12 hrs. The mixture was then refluxed at 80°C for

16 hrs brought to room temperature and filtered. Most of the solvent was removed from the filtrate under reduced pressure and the oily liquid obtained was poured into an excess hexane (300 ml). Reprecipitation was carried out by dissolving the polymer in a minimum THF (5ml) and then adding excess fresh hexane(300ml). The pale yellow crystalline solid was separated by filtration and the material was vacuum dried (2.4g, 61%).

(Since polydichlorophosphazene is very sensitive to atmospheric moisture the whole reaction was carried out in nitrogen atmosphere).

Infrared (cm^{-1}) : 1570(s), 1410(m), 1300(m), 1200(br), 1080(s), 960(s), 830 (s), 800(s), 750(s).

^{1}H NMR(δ) : 2.1 (d, 12H, CH_3), 5.8(s, 2H, CH)

^{31}P NMR (δ) : -1.2 (s, 1P,$P(Pz)_2$)

4.6 Synthesis of Coordination Compounds :

The coordination compounds with formula L.MX_2 [M = Cu; X = Cl, Br), Co (X = Cl)] where L = DIAMPZ, TETPZ, PPHVB, POLYM 1 and CAPYP were prepared by stirring appropriate ligand in dichloromethane with anhydrous metal halide. After all the metal halide had dissolved in dichloromethane the reaction mixture was filtered and evaporated to near dryness. Addition of excess hexane yielded the metal complexes in high yields. The complexes thus obtained were recrystallized from 1 : 1 solvent mixture of dichloromethane and hexane.

$$L + MX_2 \longrightarrow L \cdot MX_2$$

For L.2MCl_2 [M = Cu (X = Cl, Br)] where L = PPHVB a similar procedure was used with 2 equivalents of metal halide.

$$L + 2MX_2 \longrightarrow L \cdot 2MX_2$$

4.6.1 Illustrative Procedures

4.6.2 DIAMPZ.$CuBr_2$

To solution of DIAMPZ (0.3g, 0.5mmol) in 40 ml dichloromethane, anhydrous copper bromide (0.1g, 0.5mmol) was added. The suspension was stirred for 6hrs. The resulting green solution was filtered to remove unreacted $CuBr_2$ and concentrated in vacuum. Addition of hexane (20ml) afforded a green solid identified as DIAMPZ.$CuBr_2$ (0.3g, 81%.)

Melting point : 181 °C

Infrared (cm^{-1}) : 3340(s), 3220(s), 2860(m), 1560(s), 1450(s), 1370(vs), 800(s)

760(s)

4.6.3 DIAMPZ.$CoCl_2$

To a stirred solution of DIAMPZ (0.3g, 0.5mmol) in 40ml dichloromethane, $CoCl_2$ (71.0mg, 0.3mmol) was added and the resulting solution was stirred at room temperature for 8hrs. The dark blue solution was filtered to remove unreacted $CoCl_2$. The filtrate was concentrated to 3ml, and precipitated by adding excess hexane (20ml). The blue solid obtained was separated by filtration and dried in vacuum (0.25g, 67%).

Melting point : 284°C(dec)

Infrared(cm^{-1}) : 3340(br),3320(s), 2980(m), 2960(m), 1660(s), 1460(s), 1370 (s), 1260(s), 1150(s), 820(m), 700(s)

Elemental Analyses : Anal. calc. for $C_{20}H_{32}N_{13}P_3Cl_2Co$: C,35.46; H, 4.76; N, 26.88; Found: C, 35.23; H, 4.94; N, 27.11

4.6.4 TETPZ.$CuCl_2$

To a solution of $N_4P_4Pz_8$ (0.3g, 0.3mmol) in 25ml dichloromethane, anhydrous $CuCl_2$ (0.03g, 0.3mmol) was added. The suspension was stirred at room temperature for 5hrs. The yellow green solution was filtered and concentrated to 3ml. The metal complex was precipitated by adding an excess of hexane (20ml). The pale green solid was separarted by filtration and dried *in vacuo.* (0.19g, 55%)

Melting point : 138°C

Infrared (cm^{-1}) : 2960(br), 2930(m), 2860(s), 1560(br), 1460(s), 1450(s), 1370(s), 1040(m), 800(br), 720(m)

(Sample was recrystallized and was found to be a dimeric compound(*videsupra*)

4.6.5 TETPZ.$CuBr_2$

To a stirred solution of $N_4P_4Pz_8$ (0.3g, 0.3mmol) in dichloromethane, anhydrous $CuBr_2$ (0.06g, 0.3mmol) was added. The suspension was stirred at room temperature for 5hrs. The dark brown solution obtained was concentrated to 5ml and precipitated by adding

excess hexane(20ml). The dark brown solid was filtered and dried in vacuum. (0.24g, 73%).

Melting point : 200°C(dec)

Infrared (cm^{-1}) : 2960(m), 2920(m), 2860(br), 1560(s), 1520(s),1460(s), 1410(s), 1370(s), 1300(s), 1280(s), 1150(s), 1030(s), 850(br), 780(s)

(Satisfactory CHN analysis could not be obtained for this product as attempts to do so always resulted in decomposition of the material.)

4.6.6 TETPZ.$CoCl_2$

To a stirred solution of $N_4P_4Pz_8$ (0.3g, 0.3mmol) in 40ml dichloromethane, $CoCl_2$ (41.0mg, 0.3mmol) was added and the resulting solution was stirred at room temperature for 14hrs. The dark blue solution was filtered to remove unreacted $CoCl_2$. The filtrate was concentrated to 3ml, and precipitated by adding excess hexane (20ml). The blue solid obtained was separated by filtration and dried in vacuum (0.15g, 47%).

Melting point : 250°C(dec)

Infrared(cm^{-1}) : 3320(s), 2980(m), 2960(m), 2860(s), 1660(s), 1460(s), 1370 (s), 1270(s), 1150(s), 1040(s), 820(m), 700(s), 660(s)

(This product upon recrystallization completely decomposed and the crystals obtained were identified as $CoCl_2.Pz_2$)

4.6.7 PPHVB.$CuCl_2$

To a stirred solution of PPHVB (0.16g, 0.2mmol), anhydrous $CuCl_2$ (26.0mg,0.2 mmol) was added. The suspension was stirred at room temperature for 8hrs. The green solution was filtered to remove unreacted $CuCl_2$. The solvent was evaporated to near dryness and excess hexane (20ml) was added to precipitate PPHVB.$CuCl_2$ complex. The light green solid was separated by filtration and dried in vacuum (0.14g, 75%).

Melting point : 150°C

Infrared (cm^{-1}) : 1570(s), 1490(s), 1410(m), 1290(m), 1240(m), 1190(m),1050 (m), 960(br), 820(s)

Elemental Analyses : Anal. calc. for $C_{39}H_{46}N_{13}P_3OCl_2Cu$: C,49.80; H, 4.93; N, 19.36; Found: C, 49.61; H, 4.31; N, 19.58

4.6.8 PPHVB.2$CuCl_2$

To a stirred solution of PPHVB (0.16g, 0.2mmol) in dichloromethane (40ml) was added anhydrous $CuCl_2$ (52.0mg, 0.2mmol). The suspension was stirred for 12hrs . The resulting green solution was filtered to remove the unreacted $CuCl_2$ and concentrated to about 2ml *in vacuo*. Addition of hexane (20ml) afforded a green solid which was filtered and dried in vacuum (0.18g, 84%).

Melting point : 197°C(dec)

Infrared(cm^{-1}) ; 1570(s), 1490(s), 1410(s), 1370(s),1300(m), 1240(m), 1180(br), 1050(vs), 970(m), 900(s), 880(s), 820(m), 770(vs)

Elemental Analyses : Anal. calc. for $C_{39}H_{46}N_{13}P_3OCl_4Cu_2$: C, 43.57 ; H, 4.31; N, 16.93; Found: C, 43.79; H, 4.15; N, 16.88

4.6.9 PPHVB.$CuBr_2$

To a stirred solution of PPHVB (0.16g, 0.2mmol) in dichloromethane (40ml) was added anhydrous $CuBr_2$ (44.0mg, 0.2mmol). The suspension was stirred for 14hrs. The resulting dark yellow solution was filteres to remove unreacted $CuBr_2$ and concentrated to about 5ml *in vacuo*. Addition of hexane (30ml) afforded a yellow solid which was filtered and dried in vacuum (0.17g, 83%).

Melting point : 161°C

Infrared (cm^{-1}) ; 2960(br), 2880(m), 1570(s), 1490(vs), 1460(m), 1370(m), 830(m), 720(m)

Elemental Analyses : Anal. calc. for $C_{39}H_{46}N_{13}P_3OBr_2Cu$: C, 45.50; H, 4.50; N, 17.68; Found: C, 45.73; H, 4.37; N, 17.91

4.6.10 PPHVB.2$CuBr_2$

To a stirred solution of PPHVB (0.16g, 0.2mmol) in dichloromethane(40ml) was added $CuBr_2$ (88.0mg,0.4mmol). The suspension was stirred for 12hrs. The resulting dark yellow solution was filtered to remove unreacted $CuBr_2$ and concentrated to about 5ml *in vacuo*. Addition of hexane (30ml) afforded a yellow solid which was filtered and dried in vacuum (0.28g, 80%).

Melting point : 160°C(dec)

Infrared (cm^{-1}) : 2980(m), 2970(br), 2860(s), 1570(s), 1460(br), 1370(m), 1240(m), 1190(br), 1050(m), 830(m)

Elemental Analyses : Anal. calc. for $C_{39}H_{46}N_{13}P_3OBr_4Cu_2$: C, 37.39; H, 3.70; N, 14.53; Found: C, 37.59; H, 3.63; N, 14.89

4.6.11 POLYM1. $CuCl_2$

To a stirred solution of POLYM 1 (0.16g, 0.2mmol) in dichloromethane (40ml) was added anhydrous $CuCl_2$ (26.0mg, 0.2mmol). The suspension was stirred for 12 hrs. The resulting green solution was filtered to remove unreacted $CuCl_2$ and concentrated to about 5ml *in vacuo*. Addition of 30ml of hexane afforded a green solid which was filtered and dried in vacuum (0.12g, 64%).

Melting point : 272°C(dec)

Infrared(cm^{-1}) : 2960(br), 2880(s), 1570(s), 1490(s), 1460(br), 1410(s),137 0(m), 1230(br), 1050(br), 900(br), 1050(br), 820(m), 790(s), 720(m), 700(br).

(Attempts to obtain elemental analysis were not succesful as the polymer burned poorly and reproducible results were not forthcoming)

4.6.12 CAPYP.$CuCl_2$

To a stirred solution of CAPYP(0.05g, 0.2mmol) in dichloromethane (50ml) was added anhydrous $CuCl_2$ (0.03g, 0.2mmol). The suspension was stirrred for 12hrs. The result-

ing dark green solution was filtered to remove the unreacted $CuCl_2$ and concentrated to about 5ml *in vacuo*. Addition of hexane (40ml) afforded a dark green solid (41.0mg, 52%).

Melting point : 270°C(dec)

Infrarerd (cm^{-1}) :3320(s), 2960(m), 1560(br), 1450(s), 1300(m), 960(s), 800(s)

4.7 Results and Discussion :

4.7.1 Synthesis and Characterization of Ligands DIAMPZ, TETPZ, PPHVB, POLYM 1 and CAPYP

The reaction schemes employed to synthesize the ligands are depicted in Figure 4.5. Hexachlorocyclotriphosphazene reacts with six equivalents of 3,5-dimethylpyrazole in the presence of triethyl amine as the hydrogen chloride acceptor in benzene to yield hexakis(3,5-dimethyl-1-pyrazolyl)cyclotriphosphazene (HDPCTP). DIAMPZ has been obtained by a two step method. Aminolysis of $N_3P_3Cl_6$ by ammonia afforded geminal-2,2-diamido-4,4,6,6-tetrachloro cyclotriphosphazene [15]. This on further treatment with 3,5-dimethyl pyrazole in the presence of triethyl amine as hydrogen chloride scavenger leads to the desired ligand DIAMPZ. TETPZ is synthesized by reacting $N_4P_4Cl_8$ with 3,5-dimethyl pyrazole in presence of triethyl amine in benzene. PPHVB was synthesized by a multi step reaction as shown in Figure 4.5. PPHVB was homopolymerized at 70°C in presence of AIBN to afford POLYM 1. CAPYP was produced by reacting polydichloro phosphazene with 3,5-dimethyl pyrazole. The ligands have been characterized by multinuclear NMR , IR and also single crystal x-ray diffraction was carried out on HDPCTP.

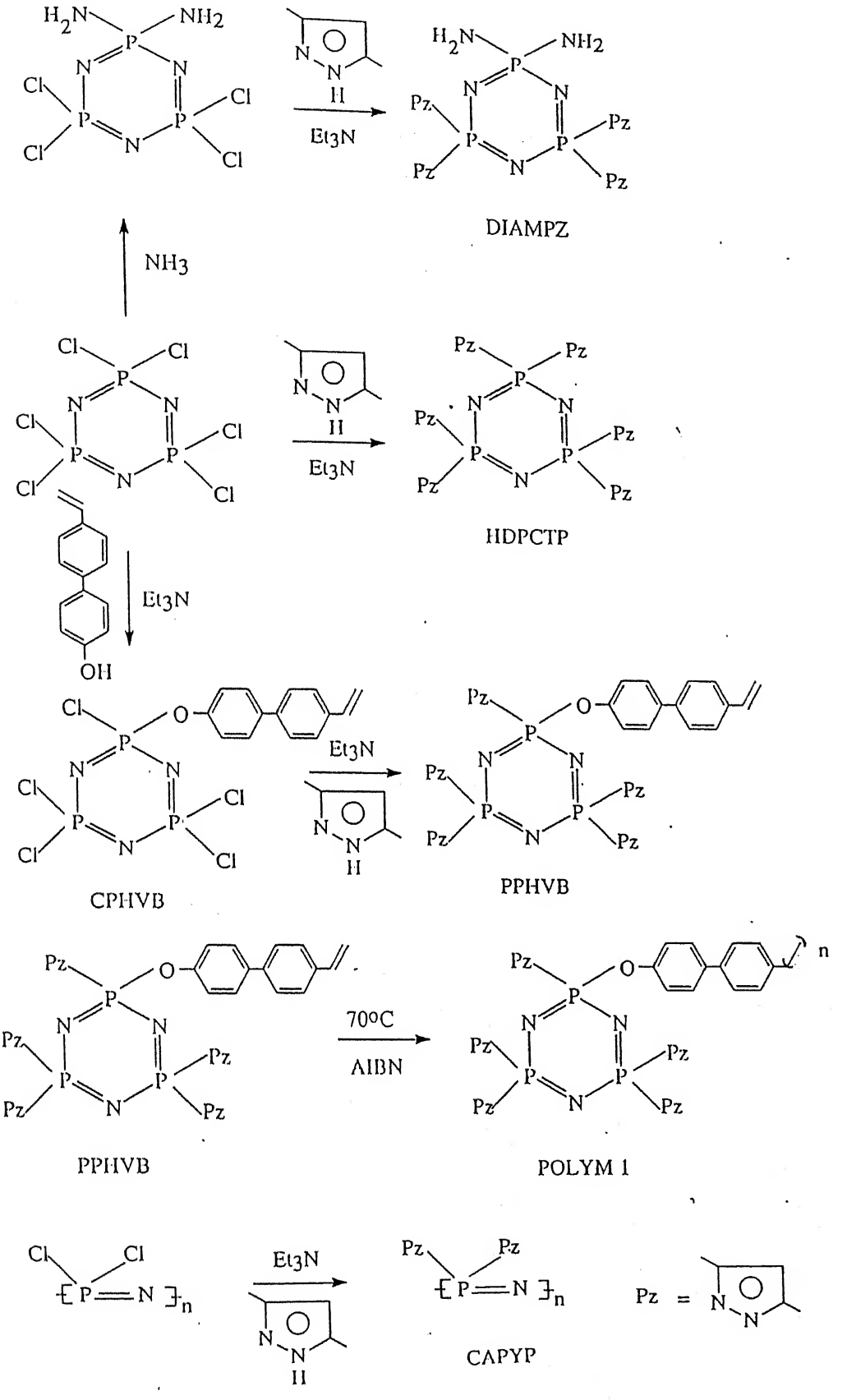


Figure 4.5: Synthesis of Ligands; Reaction Pathways.

The Mass spectra of DIAMPZ, TETPZ and PPHVB show strong parent ion peaks. Mass spectra of PPHVB is given in Figure 4.6

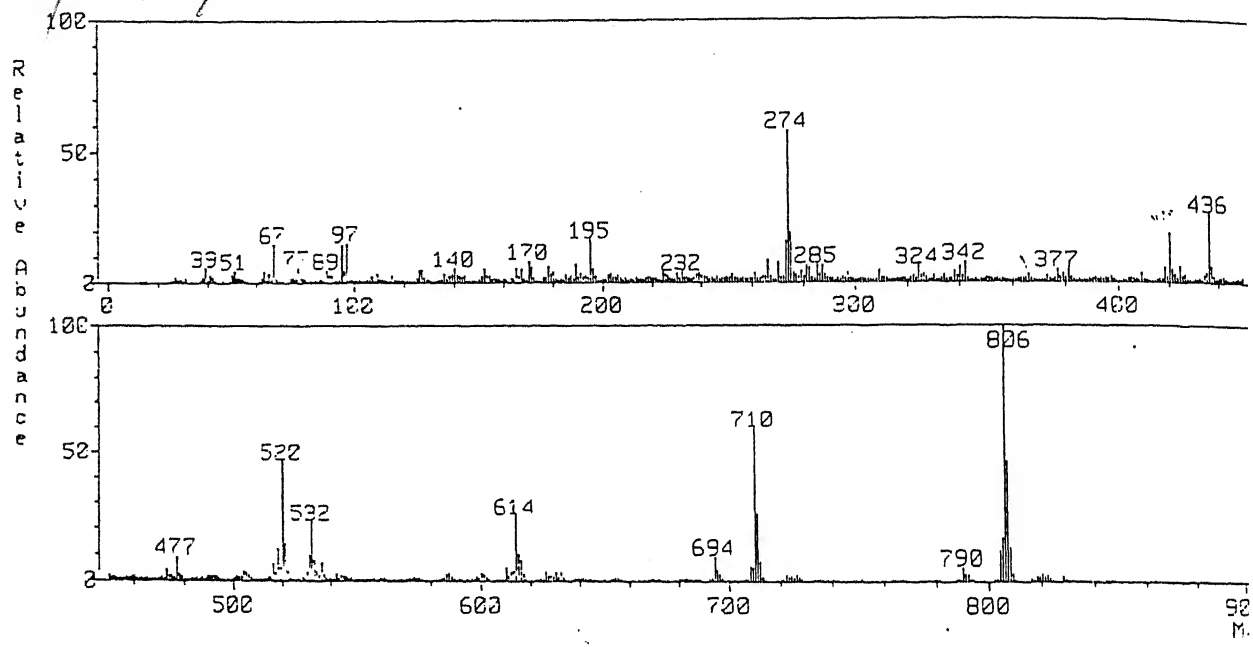


Figure 4.6: Typical FAB Mass Spectrum of PPHVB.

The proton NMR spectra of the ligands are dominated by the pyrazolyl protons. Linkage with cyclotriphosphazene phosphorus *via* N-1 causes them to be inequivalent, and two separate singlets are observed for the methyl substituent s in carbon-3 and carbon-5 in all the ligands. The proton attached to the pyrazole nucleus at carbon-4 resonates around 5.6 ppm. The ligand DIAMPZ, PPHVB and POLYM 1 show additional feature due to the phenyl, vinyl and amino groups. The proton NMR spectrum of PPHVB (Figure 4.7) shows a cluster of signals in the region 7.2-7.7 ppm and a doublet of doublet in the region 2.2-6.8 ppm for the vinyl group.Where as in TETPZ and DIAMPZ only one type of pyrazolyls are present as shown by *two* resonances for methyls, in PPHVB a cluster of methyl resonances are seen around 2.0 ppm (Table 4.1). DIAMPZ shows a broad signal at 3.3 ppm for NH_2 protons.

Table 4.1. ^{1}H NMR Data for the Pyrazolyl Ligands.

Compounds	δ Pz (3-CH_3)	δ Pz (5-CH_3)	δ Pz (4-CH)	δ Ph	δ Vinyl	δ NH_2	Ref.
PPHVB	2.1[a]	2.1[a]	6.7	7.4	5.5	-	This work
DIAMPZ	2.0	2.1	5.8	-	-	3.3	This work
TETPZ	2.0	2.1	5.6	-	-	-	This work
HDPCTP	2.22	2.3	5.5	-	-	-	16
STDPCTP	1.97	2.05	5.73	-	-	3.70	16
TDPCTP	2.15	2.26	5.88	7.3	-	-	16

[a] Multiplets observed.

The ^{31}P NMR of DIAMPZ and PPHVB display two resonances at 1.5 and 18.2 and at 0.4 and 3.1 respectively. The low frequency doublet is readily assigned to the PPz_2 groups since the values are very close to the singlet observed for HDPCTP. Table 4.2. gives the ^{31}P NMR data for the ligands and related derivatives. Figure 4.7 shows ^{31}P NMR of PPHVB. The ^{31}P NMR spectra and the ^{1}H NMR spectra of the compounds are consistent with the structure analyzed for these molecules. In addition an X-ray crystal structure of HDPCTP was carried out. It should be mentioned that the x-ray structure of TETPZ was determined earlier.

Table 4.2 ^{31}P NMR Data for the Ligands and Related Derivatives [a].

Compound	δ PPz_2	δ PCl_2	δ P_{others}	J_{p-p}	Ref.
$N_3P_3Pz_6$	-3.4	-	-	-	This work
$N_3P_3(NH_2)_2Pz_4$	1.5	-	18.2	66.3	-do-
$N_4P_4Pz_8$	5.4	-	-	-	-do-
$N_3P_3(C_8H_{11}O)Pz_5$	0.4	-	3.1	59.9	-do-
$N_3P_3Ph_2Pz_4$	-5.4	-	20.3	25.2	16
$N_3P_3Ph_2Cl_4$	-	17.1	19.5	12.0	17
$N_3P_3Im_6$	-	-	2.3	-	28

[a] Chemical shifts are in ppm (ref : 85%H_3PO_4) and coupling constants are in Hz.

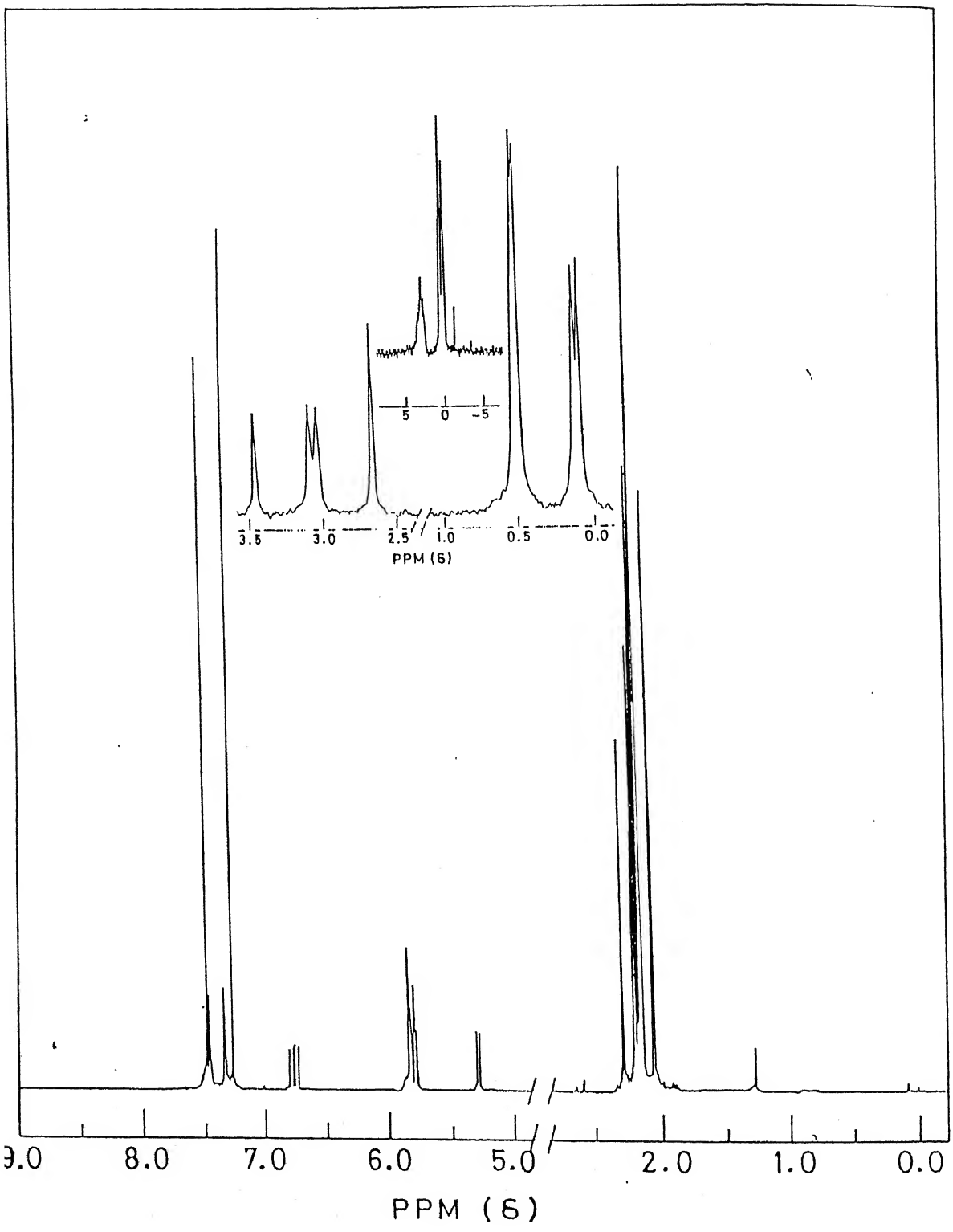


Figure 4.7: ^{1}H NMR and ^{31}P NMR Spectrum (inset) of PPHVB.

4.8 Description of Crystal Structures

4.8.1 Crystal Structure of HDPCTP

An ORTEP diagram of HDPCTP with atomic numbering scheme is presented in Figure 4.8. The six membered phosphazene ring in HDPCTP is planar. The six pendant pyrazolyl units are also planar. A tabulation of bond distances and and bond angles is shown in Table 4.3 The various phosphorus-nitrogen bond distances with in the phosphazene ring are similar to each other. The average P-N bond length 1.578(2)$\AA$ is comparable to phosphorus-nitrogen bond distances reported for other symmetrically substituted cyclotriphosphazenes (*see Table 4.4*). The endocyclic N-P-N bond angles averaged to 118(2)° and the P-N-P angles to 121(2) °. These angles are comparable to those reported elsewhere for other related compounds (Table 4.4). The average exocyclic phosphorus-nitrogen bond length is 1.685(3)$\AA$ in this structure. This suggests that these bonds have more single bond character than those with in the phosphazene ring. This value is reminiscent of a number of other exocyclic phosphorus-nitrogen bond lengths that have been reported.

4.8.2 Bonding with in the Pyrazole Rings :

The pyrazole groups are aromatic in character. The average bond distance with in each pyrazole group is 1.39(3) $\AA$. The amino nitrogen (bound to phosphorus) lone pair electrons can be delocalized into phosphazene ring in (alkylamino) or (arylamino) phosphazenes. However, in HDCTP the lone pairs are delocalized into the aromatic π system of the pyrazole substituents. Hence, these lone pair electrons can not enhance the electron density on the skeletal phosphorus or nitrogen atoms in a way that would inhibit hydrolysis reactions. This also suggests that the second nitrogen atom may constitute an alternative site for protonation. Although it would have been desirable to compare the crystal structure of HDPCTP with that of TETPZ, unfortunately details about the x-ray structure of the latter are very few. However, it is to be noted that

in TETPZ the endocyclic P-N bond lengths (avg) is quite short at 1.557 $\AA$. Similarly the exocyclic P-N bond length 1.691$\AA$ is one of the longest known in cyclophosphazene literature for a P-N bond length. The authors also comment on the resemblence of the 3,5-dimethylpyrazolyl substituents with that of an electron withdrawing chlorine rather than a methyl substituent.

Table 4.3 Selected Bond Distances(a) and Bond Angles (b) in HDPCTP.

(a)	
P(1)-N(1) 1.61(3)	P(1)-N(3) 1.55(3)
P(1)-N(11) 1.71(3)	P(1)-N(21) 1.66(3)
P(2)-N(1) 1.55(1)	P(2)-N(2) 1.57(3)
P(2)-N(31) 1.62(3)	P(2)-N(41) 1.66(4)
P(3)-N(2) 1.59(3)	P(3)-N(3) 1.60(1)
P(3)-N(51) 1.70(4)	P(3)-N(61) 1.76(3)
N(11)-N(12) 1.33(3)	N(11)-C(15) 1.34(3)
N(11)-C(15) 1.34(3)	N(12)-C(13) 1.42(4)
N(12)-C(13) 1.42(4)	C(13)-C(14) 1.45(4)
C(13)-C(16) 1.30(4)	C(14)-C(15) 1.45(4)
(b)	
N(1)-P(1)-N(3) 118 (9)	N(1)-P(1)-N(11) 109(2)
N(1)-P(1)-N(21) 109(2)	N(3)-P(1)-N(11) 107(2)
N(3)-P(1)-N(21) 110(2)	N(11)-P(1)-N(21) 101(1)
N(1)-P(2)-N(2) 119(2)	N(1)-P(2)-N(31) 111(1)
N(1)-P(2)-N(41) 105(2)	N(2)-P(2)-N(31) 107(2)
N(2)-P(2)-N(41) 111(2)	N(31)-P(2)-N(41) 102(2)
N(2)-P(3)-N(3) 117(2)	N(2)-P(3)-N(51) 111(2)
P(1)-N(1)-P(2) 121(2)	P(2)-N(2)-P(3) 121(7)
P(1)-N(3)-P(3) 122(2)	P(1)-N(21)-N(22) 114(2)

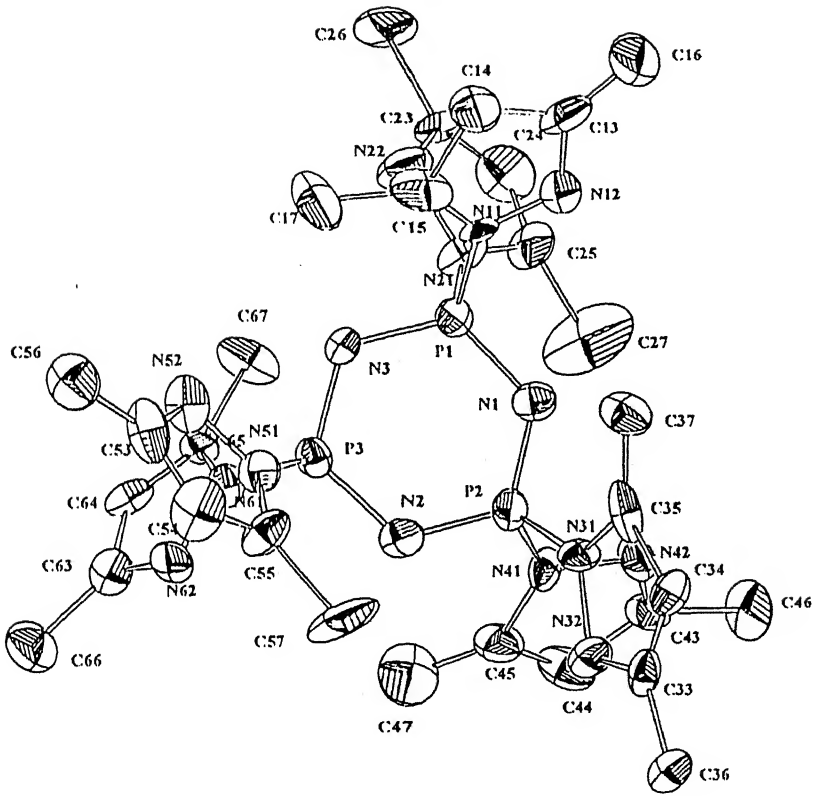


Figure 4.8: ORTEP Plot of HDPCTP.

Table 4.4: Bond Distances and Bond Angles for Various Derivatives.

compounds	Bond distances $\AA$		Bond angles °			
	P=N_{endo}	P-X_{exo}	NPN	PNP	XPX	ref.
$N_3P_3(NMe_2)_6$	1.588(3)	1.652(4)	116.7(4)	123.0(4)	101.5(8)	18
$N_3P_3(Im)_6$	1.557	1.68	119.1	120.1	102.3	19
$N_3P_3(NH(CH_2)_3NH)_3$	1.600(5)	1.656(4)	115.2(4)	122.4(3)	101.9	20
$N_3P_3Pz_6$	1.578(2)	1.685(3)	118.1(2)	121.6(2)	101.3(2)	present work

4.9 Coordination Compounds of the Ligands DIAMPZ, TETPZ, and PPHVB

4.9.1 General

The ligand DIAMPZ consists of two pyrazolyl groups less than in HDPCTP. Reduction of number of pyrazolyl groups should significantly affect the coordination response of DIAMPZ as it can bind only one metal as an N_3 donor in its non-geminal interaction mode. However, in favorable circumstances a bis(bidentate) chelation *via* geminal N_2 is possible. An additional coordination possibility does exist *via* the amido nitrogens. DIAMPZ in its reactions with copper and cobalt salts affords a variety of mononuclear coordination compounds. Table 4.5 summarizes the physical characteristics of these derivatives. The ligand TETPZ is a potential multidentate ligand with three bond bites built in between the donor atoms if the coordination is *via* nongeminal pyrazolyl substituents and cyclophosphazene skeletal nitrogen. On the other hand, geminal coordination to metal without phosphazene ring nitrogen participation may lead to six-membered chelate complexes with bidentate ligation per metal. Either way the ligand is capable of carrying four metals [in a tetrakis (tridentate) or tetrakis (bidentate) fashion.PPHVB has five pyrazolyl units and therefore is very similar to the hexakis derivative (HDPCTP) and would be expected to coordinate in a similar way.

Table 4.5: Physical Characteristics of Coordination Compounds Under Taken in this Thesis.

Compound	Color	Nature	μ_{eff}(BM)	Λ_m [a]
DIAMPZ.$CuBr_2$	green	crystalline	1.62	17.49
DIAMPZ.$CoCl_2$	dark blue	crystalline	3.74	18.3
TETPZ.$CuCl_2$	light-green	crystalline	1.98	15.48
TETPZ.$CuBr_2$	brown	powder	1.71	40.90
TETPZ.$CoCl_2$	blue	crystalline	-	31.15
PPHVB.$CuCl_2$	light-green	powder	1.74	22.51
PPHVB.2$CuCl_2$	light-green	powder	1.78	25.53
PPHVB.$CuBr_2$	yellow	powder	1.91	31.05
PPHVB.2$CuBr_2$	dark-yellow	powder	2.05	14.77
POLYM 1.$CuCl_2$	light-green	powder	1.85	2.92
CAPYP.$CuCl_2$	dark-green	crystalline	1.96	32.06

[a] unit = mho cm^2 mol^{-1}

The reactions of Cu(II)X_2(X = Cl, Br) and $CoCl_2$ with the ligands TETPZ, DIAMPZ and PPHVB in dichloromethane in a 1 : 1 or 1 : 2 molar ratio yield the mono and dimetallated derivatives. Conductivity data (*see Table 4.5*) for them in acetonitrile clearly indicate that the halides are bound to copper and cobalt in the coordination sphere, while the magnetic moment data (*see Table 4.5*) rule out any significant magnetic interaction between the metal centers in the 1 : 2 compounds and suggests that 1 : 1 compounds are monomeric in nature. The infrared spectra of all the above compounds show the presence of ligand bands. It is known that metallation or protonation of ring nitrogen atoms in cyclophosphazene leads to a splitting of the ring P=N streching frequency, which is observed usually between 1190 and 1300cm^{-1}. This splitting is ascribed to the unequal P=N bond distances with in the cyclophosphazene ring [18]. On the contrary if coordination is exclusively through exocyclic atoms the P=N streching frequency remains largely unaffected. All the complexes studied in the present thesis showed splitting in the region, thus indicating the participation of

cyclophosphazene ring nitrogen in coordination.

4.9.2 Electronic Spectra

The electronic spectra of copper complexes are summarized in Table 4.6.

Table 4.6: Electronic Spectral Data for Mononuclear and Homodinuclear Complexes of PPHVB.

Compound	solvent	$\lambda_{max}(\varepsilon max)$	assignment
PPHVB.$CuCl_2$	$CHCl_3$	878.0(2.44)	d-d
		897.0(2.69)	d-d
		350.0(3.37)	Pz-Cu l.m.c.t.
		283.0(4.47)	Pz-Cu l.m.c.t.
		232.0(4.47)	π-π^* intra ligand
PPHVB.2$CuCl_2$	$CHCl_3$	875.0(2.65)	d-d
		841.0(2.68)	d-d
		361.0(3.57)	Pz-Cu l.m.c.t.
		282.0(4.55)	Pz-Cu l.m.c.t.
		233.0(4.56)	π-π^* intra ligand
PPHVB.$CuBr_2$	$CHCl_3$	896.0(2.76)	d-d
		423.0(3.40)	Pz-Cu l.m.c.t.
		388.5(2.75)	Pz-Cu l.m.c.t.
		283.0(4.50)	Pz-Cu l.m.c.t.
		232.0(4.54)	π-π^* intra ligand
PPHVB.2$CuBr_2$	$CHCl_3$	861.0(2.84)	d-d
		841.0(2.85)	d-d
		424.0(3.35)	d-d?
		279.0(4.50)	Pz-Cu l.m.c.t.
		233.0(4.63)	π-π^* intra ligand

The transitions near 280nm and 360nm are seen in all complexes. Based on the pioneering work of Schugar and *etal* [21] and later studies by Chandrasekhar and Justin Thomas these transitions can be ascribed to π_2(Pz)-Cu(II) and π_1(Pz)-Cu(II) charge transfer transitions. The band around 230nm is attributed to π-π^* intraligand transition for the bromo complexes. The transition observed near 420nm can be attributed to Br-Cu(II) l.m.c.t [22]. The presence of single d-d absorption with high energy shoulder for copper (II) complexes suggest that copper is in a trigonal bipyramidal geometry [23]. In contrast to the electronic spectra of PPHVB, Cu complexes TETPZ metal complexes owing to their decomposition in solution afford electronic spectra that are not reproducible. The electronic spectra of the cobalt complexes exhibit two prominent d-d transitions in the region 500-1000nm and a shoulder at 256nm. This suggests that the existence of equilibrium between the five coordinate trigonal bipyramidal and four coordinate tetrahedral structures.

4.9.3 EPR Spectroscopy

The EPR spectra of TBP Cu (II) complexes are characterized by an axial symmetry with $g_\perp > g_\parallel \simeq 2$. Usually a hyperfine structure is seen in $g_\parallel$ region with $A_\parallel$ being in the range $(60 - 100X10^{-4}cm^{-1})$. However, it was observed earlier for HDPCTP. $2CuCl_2$ and HDPCTP. $2CuBr_2$ these trends are reversed with $g_\parallel > g_\perp \simeq 2.0$. This was interpreted as indicative of a distorted trigonal bipyramidal geometry around copper. X-ray crystal structure confirmation was also obtained. In the present instance also the EPR spectra of PPHVB. $CuCl_2$, PPHVB. $2CuCl_2$ and PPHVB. $2CuBr_2$ are of the axial type with $g_\parallel > g_\perp$. These values are listed in Table 4.7. Thus it is likely that in PPHVB .CuX_2 the coordination geometry around copper is distorted TBP. Attempts to confirm this by single crystal x-ray structure were not successful as suitable crystals could not be grown. However as described *vide supra*, x-ray structure of Co complex of DIAMPZ was ~~carried out~~ determined which indicates that two exocyclic pyrazolyl nitrogens along with one cyclotriphosphazene ring nitrogen are involved in coordination to Co. It is likely that in PPHVB complexes also a similar coordination behaviour is present.

Table 4.7: EPR Data for Selected Mono and Homodinuclear Complexes of PPHVB.

Compounds	$g_{\parallel}$	$g_{\perp}$	g^{a}_{av}	ref.
PPHVB.$CuCl_2$	2.242	2.057	2.120	This work
PPHVB.2$CuCl_2$	2.187	2.114	2.139	-do-
PPHVB.2$CuBr_2$	2.144	2.053	2.074	-do-
HDPCTP.2$CuCl_2$	2.233	2.059	2.147	16
TDPCTP.$CuBr_2$	2.007	2.146	2.077	16

[a] $g_{avg} = [1/2(g_{\parallel}^2 + g_{\perp}^2]^{1/2}$

4.9.4 Crystal Structure of DIAMPZ.$CoCl_2$

The x-ray structure of the cobalt complex $N_3P_3Ph_2Pz_4$ shows that cobalt is present in a distorted tbp geometry (Figure 4.9). The axial positions are occupied by the nitrogen atoms derived from the pyrazolyl moiety. The equatorial positions are taken up by the ring nitrogen atoms of the inorganic heterocycle along with two chloride ions. The distortion of the ideal tbp geometry can be seen by the shrinkage of the N(11)-Co-N(31) angle from an ideal 180° to 160.0(2). Secondly the equatorial angles Cl(1)-Co-N(1) (101), Cl(2)-Co-N(1) (115) and Cl(1)-Co-Cl(2) (118) are all less than the ideal equatorial angle of 120°. This distortion in geometry is clearly a result of the rigid cyclophosphazene frame work. Indeed in all crystal structures of the metal complexes of pyrazolyl cyclotriphosphazenes the geometry around metal suffers a similar distortion (Table 4.9). Also in all the metal complexes (Cu(II), Co(II) and Ni(II)) of 3,5-dimethylpyrazolyl cyclotriphosphazenes a similar coordination response from the ligand is observed indicating that the steric constraints dictate the coordination response rather than electronic factors. The only exception where the equatorial positions are ~~taken up~~ occupied by pyrazolyl nitrogens is found for $N_3P_3Ph_2Pz_4.CoCl_2$ [2a]. In this example the pyrazolyl substituent does not carry the sterically hindering methyl groups. As a result of coordination the P-N bond lengths undergo significant lengthening in the segment where coordination occurs. These data along with data for related

compounds are summarized in Table 4.10. The bond length inequalities are explained by existing theories of bonding in cyclophosphazenes. Several structural studies on cyclophosphazenes have conclusively shown that either protonation or coordination of a metal to the ring nitrogen atom increases the P-N bond distances involved with that nitrogen atom. This feature has been interpreted as due to a non availability of the lone pair on the nitrogen concerned for participation in skeletal pi bonding of the inorganic ring, there by resulting in decrease in pi bond character, consequently the bonds affected by protonation or coordination to a metal are lengthened in comparison with other bond lengths. The bond lengths with in the phosphazene ring are not equal as they are in $N_4P_4(NMe_2)_8.W(CO)_4$ and $N_4P_4(Me)_8.PtCl_2$. The exocyclic P-N bond distance average to 1.68$\AA$ which is longer than for $N_4P_4(Pz)_8$ (1.578$\AA$) derivative. The endo cyclic P-N-P bon angles are shorter at N(1) and N(3) (mean 123.5°) and longer at N(2) and N(4) (mean 133.5°).

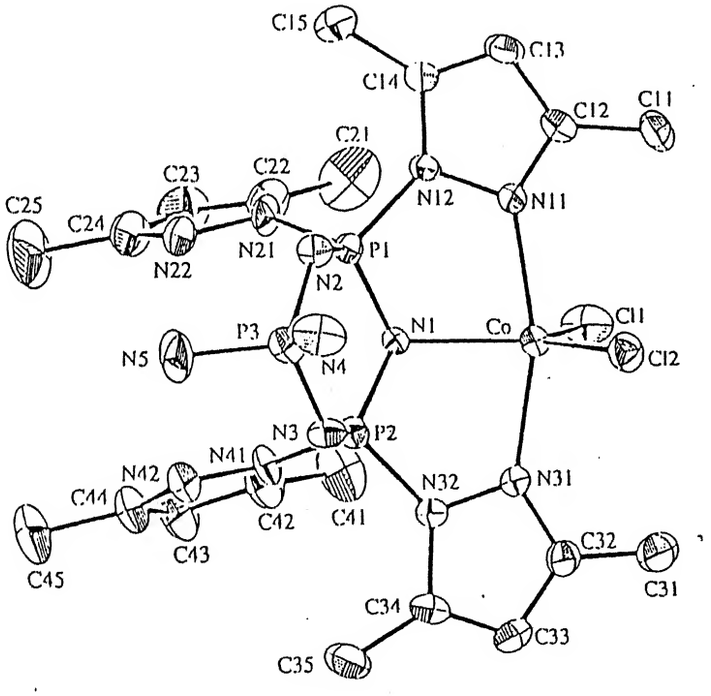


Figure 4.9: Molecular Structure of DIAMPZ.$CoCl_2$

Table 4.8: Selected Bond Distances (a) and Bond Angles (b) in DIAMPZ.$CoCl_2$

(a)	
Co-Cl(1) 2.262(2)	P(2)-N(1) 1.623(5)
Co-Cl(2) 2.296(2)	P(2)-N(3) 1.560(5)
Co-N(1) 2.117(5)	P(2)-N(32) 1.683(6)
Co-N(11) 2.114(6)	P(2)-N(41) 1.687(5)
Co-N(31) 2.120(6)	P(3)-N(2) 1.615(5)
P(1)-N(1) 1.608(5)	P(3)-N(3) 1.620(6)
P(1)-N(2) 1.558(5)	P(3)-N(4) 1.637(6)
P(1)-N(12) 1.685(5)	P(3)-N(5) 1.660(6)
P(1)-N(21) 1.672(5)	N(31)-N(32) 1.380(7)
(b)	
Cl(1)-Co-Cl(2) 121.70(8)	N(11)-Co-N(31) 160.0(2)
Cl(1)-Co-N(1) 115.5(2)	N(1)-P(1)-N(2) 117.6(3)
Cl(1)-Co-N(31) 100.2(2)	N(2)-P(3)-N(3) 112.9(3)
Cl(2)-Co-N(1) 122.8(1)	N(2)-P(3)-N(4) 106.6(3)
Cl(2)-Co-N(11) 91.7(2)	N(2)-P(3)-N(5) 112.4(3)
Cl(2)-Co-N(31) 90.6(1)	N(3)-P(3)-N(4) 113.0(3)
N(1)-Co-N(31) 80.8(2)	N(3)-P(3)-N(5) 106.9(3)
N(1)-Co-N(11) 81.3(2)	N(4)-P(3)-N(5) 105.0(3)

Table 4.9: Comparison of Geometries of Selected Five-Coordinate Complexes.

Complex	Geometry	X-M-X	$M-N_{long}$	$M-N_{short}$	τ value	% tbp	Ref.
DIAMPZ	distorted	121.7(8)	2.120(6)	2.117(5)	0.74	92.5	present
$CoCl_2$	tbp			2.114(6)			work
HDPCTP	distorted	142.28(10)	2.360(5)	1.988(5)	0.31	63	24
$CuCl_2$	tbp			1.974(5)			
TDPCTP	distorted	132.21(8)	2.320(5)	1.984(5)	0.45	74	2(b)
$CuCl_2$	tbp			1.974(5)			
TPCTP	distorted	106.44(5)	2.419(3)	2.038(4)	0.74	87	2(a)
$CoCl_2$	tbp			2.062(4)			
TDPCTP	distorted	114.77(6)	2.089(4)	2.079(3)	0.53	86	25
$NiCl_2$	tbp			2.080(4)			

Table 4.10: Comparison of the Pyrazolyl Cyclotriphosphazene Structural Features.

Compounds	P=N Distance in		P-N-P Angle in		Ref.
	P-N(M)P	P-N-P	P-N(M)-P	P-N-P	
DIAMPZ.$CoCl_2$	1.608(5)	1.558(5), 1.616(5)	114.0(3)	122.7(4)	Present
	1.623(5)	1.620(6), 1.560(5)		121.2(3)	work
HDPCTP.$CuCl_2$	1.596(5)	1.564(5), 1.574(5)	118.4(3)	122.5(3)	24
	1.589(5)	1.575(5), 1.578(5)		121.3(3)	
TDPCTP.$CuCl_2$	1.601(5)	1.552(5), 1.561(5)	117.6(3)	122.1(3)	2(b)
	1.600(5)	1.614(5), 1.610(5)		123.1(3)	
TDPCTP.$NiCl_2$	1.590(4)	1.537(4), 1.537(4)	114.4(2)	120.9(2)	25
	1.591(4)	1.611(4), 1.591(4)		122.6(2)	
TPCTP.$CoCl_2$	1.586(3)	1.548(4), 1.551(4)	118.6(21)	121.25(22)	2(a)
	1.592(4)	1.615(4), 1.621(4)		122.74(23)	

Table 4.11: Comparison of Metal Environment in the PyrazolylCyclotriphosphazene Complexes.

Complexes	NPz-M-Pz	NPz-M-N_{ctp}	M-N_{ctp}	M-NPz	M-Cl	Ref.
HDPCTP	160.74(21)	81.0(18)	2.360(5)	1.984(5)	2.2676(21)	24
$CuCl_2$		80.68(19)		1.974(5)	2.2429(19)	
TDPCTP	159.39(20)	80.86(19)	2.320(5)	1.984(5)	2.2639(21)	2(b)
$CuCl_2$		80.60(19)		1.974(5)	2.2822(14)	
TPCTP	114.03(14)	77.30(13)	2.419(3)	2.038(4)	2.2709(14)	2(a)
$CoCl_2$		75.85(13)		2.062(4)	2.2859(14)	
TDPCTP	160.0(1)	80.3(1)	2.079(3)	2.080(4)	2.258(1)	25
$NiCl_2$		80.5(1)		2.089(4)	2.248(2)	
DIAMPZ	160.0(2)	81.3(2)	2.117(5)	2.114(6)	2.262(2)	present
$CoCl_2$		80.8(2)		2.210(60	2.296(2)	work

4.9.5 TETPZ.$CuCl_2$

The TETPZ.$CuCl_2$ afforded a hydrolyzed derivative $C_{30}H_{46}N_{16}O_2Cl_3P_4Cu_2$. This compound although obtained unintentionally has a number of very interesting features. It is a homo bimetallic compound with two coppers being present. The cyclophosphazene ring coordinates to the two coppers by a total of four pyrazolyl substitue nts all of which are in the same plane and two ring nitrogen atoms. Different views of this molecule are shown in Figure 4.10. The geometry around each copper is trigonal bipyramidal with the equatorial positions being described by two chlorines and a cyclophosphazene ring nitrogen atoms. The two axial positions are taken up by two pyrazolyl nitrogens. A view of the geometry around copper is provided in Figure 4.10(a). An interesting feature of this arrangement is a bridging chlorine between the two coppers. There is a difference in the bond lengths observed between copper and nitrogens depending upon the source of the nitrogen atom. Thus the Cu-N(Pz) is shorter, compared to Cu-N(ctp) (Table 4.12). Thus the axial bond angle N(22)-Cu(2)-N(42) is 163.4°(10), while the equatorial bond angles are also similarly deviated away from the

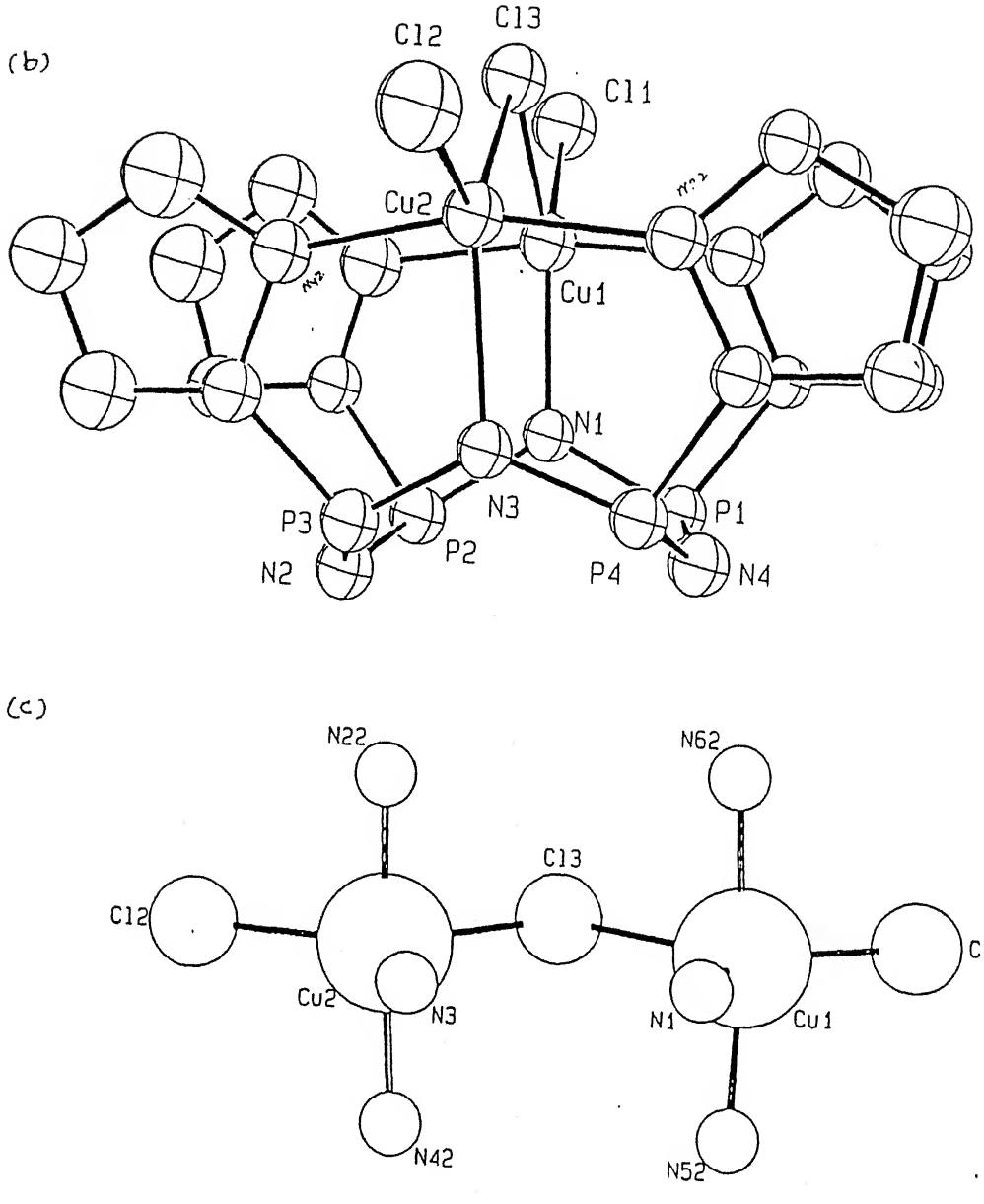


Figure 4.10 (Continued):

4.10(b) Saddle Structure of the Cyclotetraphosphazene ring

4.10(c) Copper Environment with bridged chlorine.

Table 4.12: Selected Bond Distances (a) and Bond Angles (b) in TETPZ.$CuCl_2$

(a)	
Cu(1)-Cl(1) 2.255(10)	P(4)-N(4) 1.52(3)
Cu(1)-Cl(3) 2.590(9)	P(4)-N(3) 1.584(18)
Cu(1)-N(1) 2.024(17)	P(3)-N(3) 1.596(19)
Cu(1)-N(52) 1.98(2)	P(3)-N(2) 1.49(3)
Cu(1)-N(62) 2.02(2)	P(2)-N(2) 1.63(3)
Cu(2)-Cl(2) 2.322(9)	P(2)-N(1) 1.63(2)
Cu(2)-Cl(3) 2.335(8)	P(1)-N(4) 1.60(2)
Cu(2)-N(3) 2.151(17)	P(1)-N(1) 1.611(19)
Cu(2)-N(22) 1.927(19)	Cu(2)-N(42) 1.94(2)
(b)	
Cl(1)-Cu(1)-Cl(3) 108.0(3)	Cl(1)-Cu(1)-N(1) 136.0(7)
Cl(1)-Cu(1)-N(52) 93.5((9)	Cl(1)-Cu(1)-N(62) 96.6(7)
Cl(3)-Cu(1)-N(1) 116.0(6)	Cl(3)-Cu(1)-N(52) 91.3(7)
Cl(3)-Cu(1)-N(62) 91.3(8)	N(1)-Cu(1)-N(52) 84.9(9)
N(1)-Cu(1)-N(62) 83.6(9)	N(52)-Cu(1)-N(62) 168.2(10)
Cl(2)-Cu(2)-Cl(3) 124.1(3)	Cl(2)-Cu(2)-N(3) 119.5(6)
Cl(2)-Cu(2)-N(22) 92.9(7)	Cl(2)-Cu(2)-N(42) 95.5((7)

4.9.6 Crystal Structure of $Pz_2.\ CoCl_2$

Attempts to crystallize the TETPZ.$CoCl_2$ resulted in complete hydrolysis of the cyclotetraphosphazene ligand and the crystals were identified as $Pz_2.\ CoCl_2$. The x-ray structure of this molecule shows tetrahedral arrangement of ligands around cobalt. The bond distances and bond angle data are summarized in Table 4.14. The isolation of the hydrolyzed derivative underscores the inherent instability of the cyclotetraphosphazene ligand systems, which is presumably due to the greater reactivivty of the eight membered ring in comparison with the six membered ring.

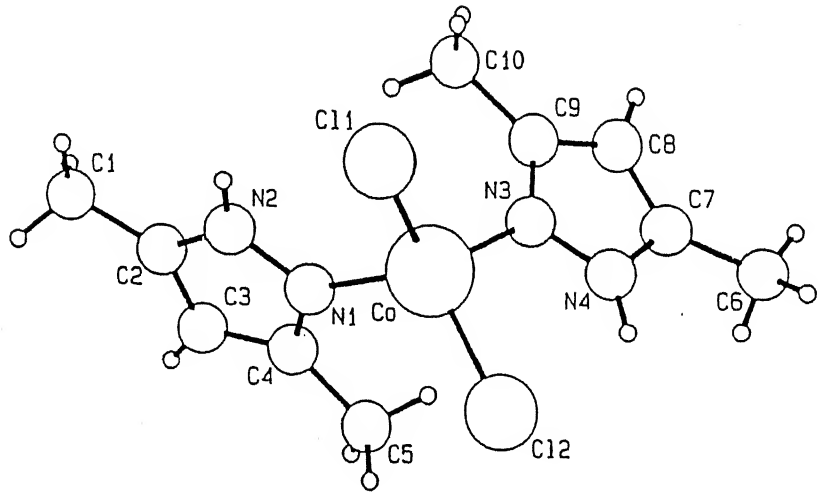


Figure 4.11: ORTEP Plot of $Pz_2.\ CoCl_2$.

Table 4.13: Crystal Data for $Pz_2.\ CoCl_2$

formula	$Pz_2.CoCl_2$
fw	320.08
crystal size, mm	0.30 x 0.32 x 0.44
crystal color	dark blue
crystal mount	on fiber with silicone rubber
a,$\AA$	14.998(3)
b,$\AA$	8.2644(15)
c,$\AA$	24.023(5)
β,deg	96.06(20)
VA^3	2961.0(10)
cell detn, refls	25
cell detn, 2θ range, deg	24-27
d(calcd), g cm^{-3}	1.445
space group	c 2/c
Z	8
linear abs coeff, mm^{-1}	1.51
scan technique	$\theta - 2\theta$
2θ (max), deg	49.8
h,k,l ranges	-17,17; 0,9; 0,28
refl meas	5138
unique refls	2600
data with I>3σI	1869
$R(F^2), Rw(F^2)$	0.043, 0.074
final diff map, eA^{-3}	-0.42, +0.4

Table 4.14: Selected Bond Distances and Bond Angles for $CoCl_2.Pz_2$.

Co-Cl(1) 2.235(14)	N(2)-C(2) 1.355(7)
Co-Cl(2) 2.233(16)	C(3)-C(2) 1.392(8)
Co-N(1) 1.996(4)	C(3)-C(4) 1.362(8)
Co-N(3) 2.008(4)	C(2)-C(1) 1.463(9)
N(1)-N(2) 1.347(6)	C(9)-C(8) 1.370(8)
N(1)-C(4) 1.340(6)	C(9)-C(10) 1.480(9)
N(4)-N(3) 1.327(6)	C(4)-C(5) 1.471(8)
N(4)-C(7) 1.344(6)	C(7)-C(8) 1.33898)
N(3)-C(9) 1.344(7)	C(7)-C(6) 1.483(8)
Cl(1)-Co-Cl(2) 117.9(6)	C(2)-C(3)-C(4) 108.2(4)
Cl(1)-Co-N(1) 101.3(12)	N(2)-C(2)-C(3) 103.7(5)
Cl(1)-Co-N(3) 115.4(12)	N(2)-C(2)-C(1) 123.1(5)
Cl(2)-Co-N(1) 115.1(12)	C(3)-C(2)-C(1) 133.2(5)
N(1)-Co-N(3) 106.1(16)	N(3)-C(9)-C(8) 109.2(5)
N(1)-N(2)-C(2) 112.9(4)	C(9)-C(8)-C(7) 107.7(5)
N(4)-N(3)-C(9) 105.1(4)	C(8)-C(7)-C(6) 132.2(5)
Co-N(3)-C(9) 132.3(4)	N(4)-C(7)-C(6) 121.9(5)
Co-N(3)-N(4) 122.3(3)	N(4)-C(7)-C(8) 105.8(5)

The polymeric ligands POLYM 1 and CAPYP have been synthesized according to the reaction shown in Figure 4.5. The ligand PPHVB could be readily homopolymerized with AIBN at 70°C in 1,2-dichloro ethane to afford a high molecular weight polymer. Dilute viscosity measurements of POLYM 1 show intrinsic viscosity 3.6cc/g . ^{1}H NMR of POLYM 1 show an absence of vinylic protons and appearance of alkyl protons in the region 1-2ppm (*see Figure 4.12*). The integrity of the cyclophosphazene ring is retained in POLYM 1 as can be inferred by the AB_2 type of ^{31}P NMR spectrum obtained for it.

The phosphazene polymer (CAPYP) obtained from the reaction between poly dichlorophosphazene and 3,5-dimethyl pyrazole is stable at room temperature. Powder x-ray diffraction studies indicate that it is highly crystalline in nature. Poly[bis(3,5-dimethyl-1-pyrazolyl)phosphazene] shows an intrinsic viscosity of 8.0g/cc indicating that it is a high molecular weight polymer. ^{1}H NMR spectrum indicates the presence of methyl protons and a signal at 5.6 for CH proton. ^{31}P NMR of CAPYP reveal that there is small amount of residual chlorines in the polymer back bone (Figure 4.13).

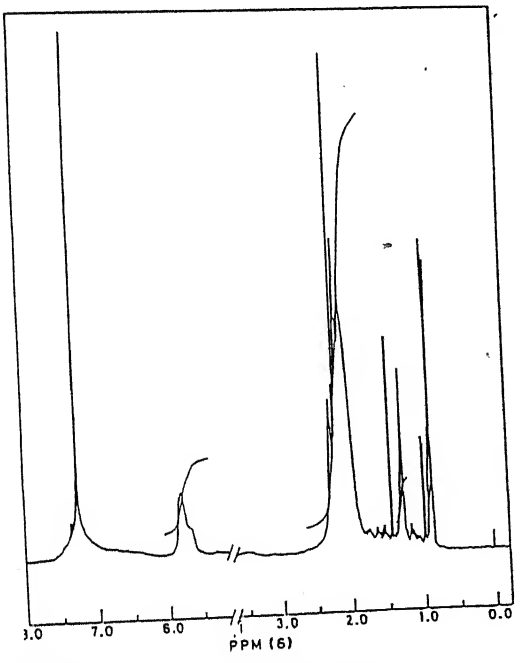


Figure 4.12: ^{1}H NMR Spectrum of POLYM 1.

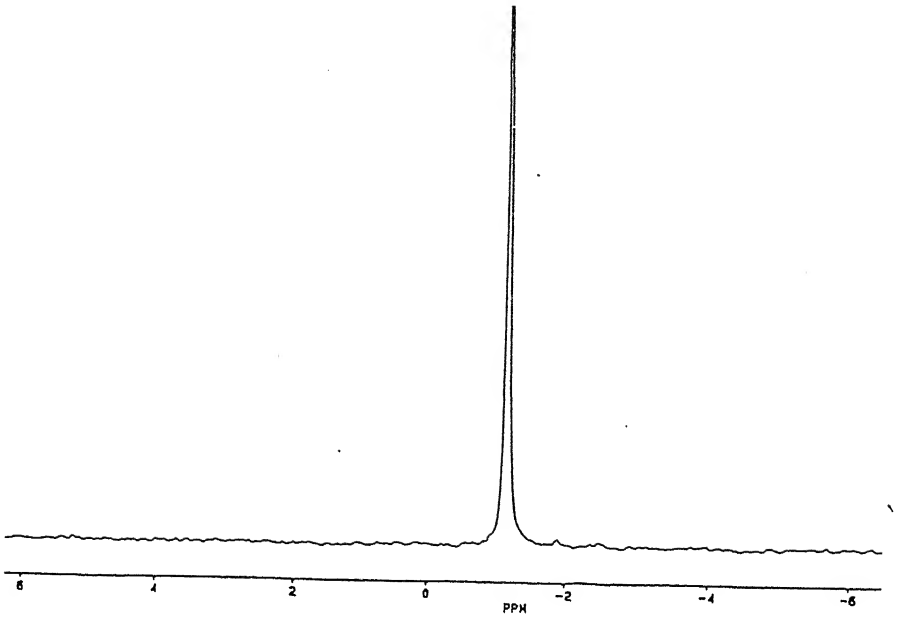


Figure 4.13: ^{31}P NMR Spectrum of CAPYP.

Differential scanning calorimetric studies indicate that these polymers have low glass transition temperature 87°C (POLYM 1) and 110°C (CAPYP) respectively. Thermal gravimetric studies indicate that POLYM 1 is thermally stable at high temperatures (Figure 4.14)and flame retardant as shown by simple flame tests. The char yield of POLYM1 (60% at 700°C)can be comparable to that of the homopolymer obtained from CPHVB (60% at 800°C). Poly[bis(3,5-dimethylpyrazolyl)]phosphazene completely decomposes at 200° C and was found to be thermally less stable.

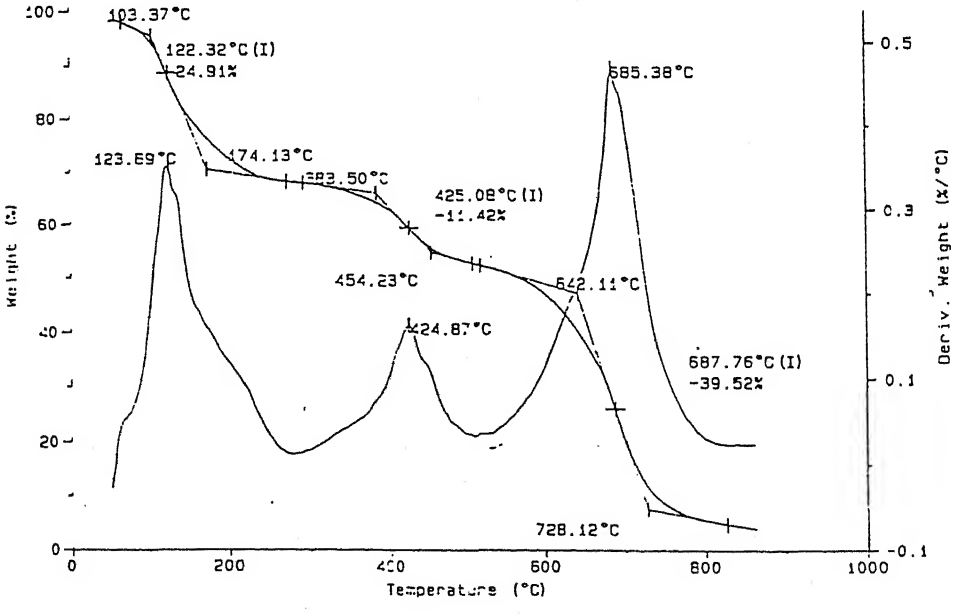


Figure 4.14: TGA Thermogram of POLYM 1.

The polymers POLYM 1 and CAPYP react with $CuCl_2$ in dichloro methane at room temperature to afford green coloured complexes. The polymeric metal complexes CAPYP.$CuCl_2$, POLYM 1.$CuCl_2$ are fairly soluble in all organic solvents. The UV-Visible spectra of these compounds are given in Table.4.15. which is comparable to the complexes of the cyclic derivatives. Based in this and on the conductivity data (neutral) a coordination behaviour similar to that found for the cyclic derivatives (as discussed *vide supra*) is proposed. EPR spectra showed only isotropic behaviour. It is possible that as a result of the polymeric nature intra and inter molecular Cu-Cu interactions lead to the observed isotropic behaviour seen in these complexes.

Table 4.15 Electronic Spectral Data for Polymeric Metal Complexes

Compound	solvent	λ_{max}(εmax)	assignment
POLYM 1.$CuCl_2$	$CHCl_3$	265.5(2.83)	Pz-Cu l.m.c.t.
		350.0(3.37)	Pz-Cu l.m.c.t.
		234.5(3.21)	π-π^* intra ligand
		368.5(2.16)	Pz-Cu l.m.c.t.
CAPYP.$CuCl_2$	$CHCl_3$	273.0(2.31)	Pz-Cu l.m.c.t
		243.0(3.44)	π-π^* intra ligand
		374.0(1.83)	Pz-Cu l.m.c.t.

4.10 Conclusions

1. A new class of cyclophosphazene based multisite transition metal interacting ligands have been synthesized using a variety of stratagies. These include bis(diamido) tetrakis(3,5-dimethyl pyrazolyl)cyclotriphosphazene (DIAMPZ), the cyclotetraphosphazene system (TETPZ) and a polymerizable cyclophosphazene ligand (PPHVB). PPHVB contains a vinyl biphenyloxy moiety anchored to the cyclophosphazene ring with the vinyl portion being intact. The coordination sites are provided through the pyrazolyl substituents. Polymeric ligands based on the above systems have also been assembled. All of these have been characterized by multinuclear NMR and other spectroscopic techniques.

2. The ligand DIAMPZ act as a tridentate ligand coordinating through two nongeminal pyrazolyl nitrogens and one cyclotriphosphazene nitrogen as confirmed by the crystal structure determination of DIAMPZ.$CoCl_2$.

3. PPHVB interacts in a similar nongeminal N_3 coordinating mode as found for DIAMPZ and other pyrazolyl cyclophosphazene ligands.

4. TETPZ is extremely sensitive to hydrolysis particularly after metallation; an unususl bimetallic copper complex has been isolated. Attempts to obtain a cobalt complex however, resulted in complete hydrolysis and only $CoCl_2.Pz_2$ was isolable.

5. The polymeric ligands derived from PPHVB (POLYM 1) and CAPYP both were found to interact with copper halides readily. From their optical spectroscopic data it was possible to show that the coordination around copper is probably similar to what was observed for the small cyclic molecules. Further studies in this area should focus on the catalytic properties on these polymeric complexes. Particularly interesting would be organic reactions involving copper such as cyclopropanation etc. .

4.11 References

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Summary

Cyclophosphazenes are among the most important inorganic heterocyclic compounds known in literature. The chemistry of these ring systems has become important in view of the facile ring opening polymerization of the six membered ring, hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ into the linear polymer, polydichlorophosphazene, $[NPCl_2]_n$ *via* a thermal polymerization route.

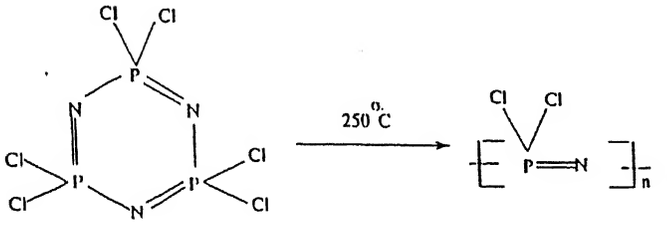

Figure 1: Thermal Polymerization of $N_3P_3Cl_6$.

Although the linear polydichlorophosphazene is a high molecular weight polymer it is hydrolytically not stable and therefore its applications are limited. However, its reactivity affords a window for the preparation of a wide range of inorganic polymers by nucleophilic substitution of chlorines in the macromolecule.

Apart from the polymerization reactions, cyclophosphazene chemistry has become interesting in view of the regio and stereo selectivities exhibited in the reactions of halogenocyclophosphazenes in various nucleophilic substitution reactions. Another facet of these ring systems is their ability to participate in interaction with transition metals *via* the skeletal nitrogen atoms of the cyclophosphazene ring and/or appropri-

ately substituted exocyclic donor substituents (groups) on the phosphorus atom of the inorganic heterocycle. In addition, in recent years, studies involving the cyclophosphazene moiety as a pendant group in the backbone of an organic polymer also are attracting attention. This thesis explores many of the above themes.

The thesis contains four chapters.

Chapter one gives an overall review on cyclo and polyphosphazene literature. The reactions of halogenocyclophosphazenes with various nucleophiles in general and amines in particular have been covered. The various stereo selectivities observed in the aminolysis of halogenocyclophosphazenes and the reaction mechanisms involved are described. Also covered are the structural aspects of cyclophosphazenes with particular emphasis on phosphorus-31 NMR and single crystal x-ray methods. The diverse coordination chemistry of various cyclophosphazenes known in literature has also been reviewed.

The various methods of polymerization of $N_3P_3Cl_6$ into the linear polyphosphazene and the subsequent assembely of a variety of polyphosphazenes is described in detail. A structure-property relationship correlation is given. Thus while the polyphosphazene with only trifluoroethoxy substituents $(NP(OR)_2)$ R = CH_2CF_3 is hydrophobic(and elastomeric), the analogous derivative with R = $CH_2CH_2OCH_2CH_2OCH_3$ is hydrophilic and water soluble besides having one of the lowest glass transition temperatures known viz Tg = - 80°C. Incidentally this latter polymer called by its acronym MEEP (methoxy ethoxy ethoxy polyphosphazene) has been found to be an excellent candidate as a polymer electrolyte.

Other methods of polymerization to afford cyclophosphazenes such as the condensation polymerization, used specially for the preparation of alkyl and aryl substituted polyphosphazenes also discussed. In addition, preparation of pendant cyclophosp-

hazene containing polymers are also discussed.

At appropriate places the state of knowledge on the bonding aspects of cyclo and polyphosphazenes are also presented. Finally chapter one concludes giving the scope and outlook of work carried out in the present thesis.

Chapter two describes the reactions of $N_3P_3Cl_6$, $N_4P_4Cl_8$ and the linear polymer $(NPCl_2)_n$ with cyclic amines, cyclohexylamine, cyclopentylamine and cyclopropylamine. This chapter contains a brief introduction followed by an experimental section and finally the results and discussion section.

In view of the fact that synthesis of these polyphosphazenes involves substitution of chlorines on the macromolecule, it is advantageous to obtain information on reaction conditions etc., suitable for such substitution by first carrying out the same reaction on the small molecule cyclophosphazenes. We have accordingly first studied the reactions of hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) and octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) with cyclic amines, cyclohexylamine, cyclopentylamine, and cyclo propylamine with an intention to understand the reactions conditions for complete substitution of chlorines in these compounds.

Table 1 shows the products obtained under various conditions for the reaction of $N_3P_3Cl_6$ with cyclic amines. It can be clearly seen that the major product isolated by column chromatography was the tetrakis derivative $N_3P_3Cl_2(NHR)_4$.

Table 1: Experimental Details of Reaction of $N_3P_3Cl_6$ with Cyclic Amines.

Amines	$N_3P_3Cl_6$ (moles)	RNH_2 (moles)	Et_3N (moles)	Solvent used	Yield %	Reaction condition	Product obtained
C_3H_5NH	0.014	0.086	0.086	C_6H_6	62.0	$8^a, 12^b$	d
C_5H_9NH	0.014	0.086	0.086	- do -	50.0	$12^a, 12^b$	d
- do-	0.003	0.003	0.003	- do -	22.3	$12^a, 0.6^c$	e
- do -	0.003	0.006	0.006	- do -	40.5	$12^a, 0.7^c$	e
- do -	0.003	0.009	0.009	- do -	23.8	$30^a, 0.42^c$	f
- do -	0.003	0.012	0.012	- do -	19.4	$24^a, 0.23^c$	f
- do -	0.003	0.014	0.014	- do -	29.3	$24^a, 0.70^c$	d
- do -	0.003	0.017	0.017	- do -	26.4	$24^a, 0.76^c$	d
- do -	0.003	0.029	0.029	- do -	28.6	$24^a, 0.82^c$	d
$C_6H_{11}NH$	0.006	0.034	0.034	THF	40.9	$12^a, 24^b$	d
- do -	0.014	0.086	0.086	CH_3CN	56.6	$12^a, 16^b$	d
- do -	0.014	0.086	0.086	C_6H_6	41.0	$12^a, 12^b$	d
- do -	0.006	0.057	0.057	$CHCl_3$	48.4	$6^a, 72^b$	d

[a] Reaction carried out at room temperature. [b] Reaction carried out at reflux conditions. [c] R_f Values obtained. [d] 2,2-gemdichloro-4,4,6,6-tetrakisderivatives. [e] Monosubstituted derivative. [f] structure could not be assigned.

The mass spectra of all these compounds DCHEA(598), DCPEA(542) and DCPRA (430) show strong parent ion peaks with the characteristic two chlorine pattern for the formula $N_3P_3Cl_2(NHR)_4$. The initial fragmentation in all these compounds proceeds by the loss of an amino group rather than through chlorine dissociation. The ^{31}P NMR data of all DCHEA, DCPEA and DCPRA are of AX_2 type. Table 2 summarizes the ^{31}P NMR data of these compounds with data of other related derivatives. The chemical shifts observed and the coupling constants are consistent with the geminal disposition of the amino substituent. All the cyclic amines investigated in the present study behave as sterically encumbered amines and prefer a geminal pathway. Also,

majority of the primary amines known in literature afforded geminal products at the tetrakis stage. In addition, all our reactions were carried out in the presence of a tertiary amine (triethylamine) which would accelerate a proton abstraction mechanism induced reaction.

Table 2: ^{31}P NMR data of Selected Primary Amino Derivatives of $N_3P_3Cl_6$.

Primary amino derivatives	δPCl_2 ppm	$\delta P(NRR')_2$ ppm	J_{p-p} Hz
$N_3P_3(NHPr^i)_4Cl_2$	22.2	9.4	49.4
$N_3P_3(NHBu^t)_4Cl_2$	19.7	3.9	52.6
$N_3P_3(NHC_6H_4OMe-p)_4Cl_2$	23.6	2.1	50.8
$N_3P_3(NHCH_2CH_2Cl)_4Cl_2$	24.5	13.3	50.5
$N_3P_3(NH(CH_2)_3NH)_2Cl_2$	23.1	12.3	43.7
$N_3P_3(NHC_6H_{11})_4Cl_2$	22.6	9.9	49.4
$N_3P_3(NHC_5H_9)_4Cl_2$	23.0	10.3	48.2
$N_3P_3(NHC_3H_5)_4Cl_2$	22.4	13.4	46.7

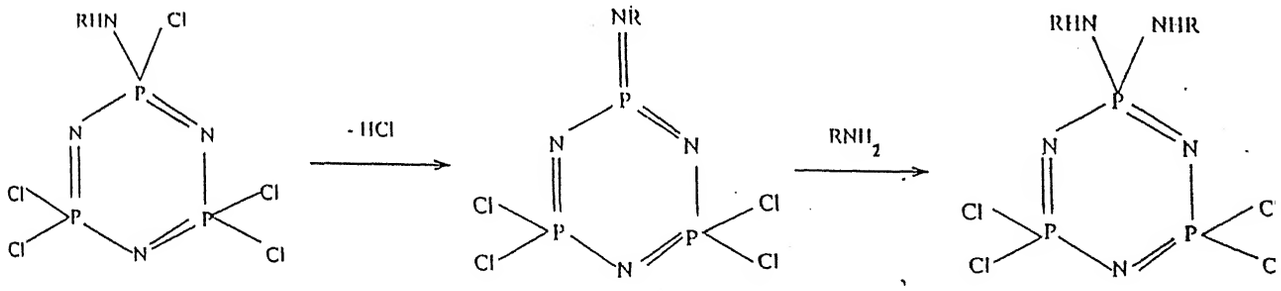

Figure 2: Proton Abstraction Mechanism.

In contrast to the reactions of cyclic amines with $N_3P_3Cl_6$, all the corresponding re-

actions with $N_4P_4Cl_8$ afford exclusively fully substituted derivatives $N_4P_4(C_6H_{11}NH)_8$ (OCHEA), $N_4P_4(C_5H_9NH)_8$ (OCPEA) and $N_4P_4(C_3H_5NH)_8$ (OCPRA). All the fully substituted derivatives are characterized readily by FAB Mass and Multinuclear NMR. The ^{31}P NMR spectra of these compounds show a single line indicating complete substitution.

The difference in reactivity behaviour between $N_3P_3Cl_6$ and $N_4P_4Cl_8$ testifies to the greater reactivity of the more flexible eight membered ring ($N_4P_4Cl_8$) compared to the relatively rigid six membered ring ($N_3P_3Cl_6$) . The x-ray crystal structures were carried out to confirm these structures.

Single x-ray crystal structural analysis of $N_3P_3Cl_2(C_6H_{11}NH)$ showed that the molecule is nearly planar with one atom N (2) being out of the plane by 0.16Å. These bond length variations are rationalised in terms of different degrees of π bonding present with in the cyclophosphazene ring.

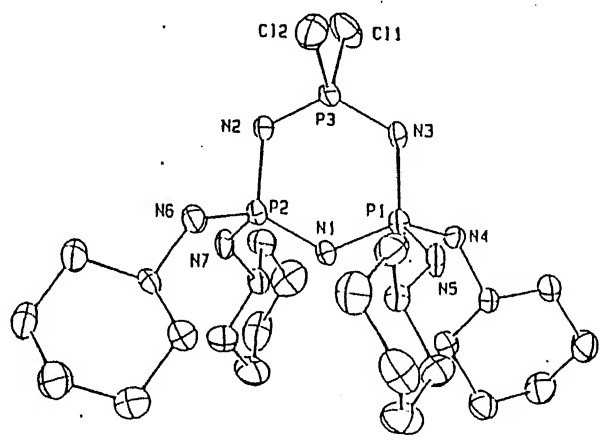

Figure 3: ORTEP diagram of DCHEA.

There are very few x-ray structures of fully substituted amino cyclotetraphosphazenes. The main feature of the structure is the presence of two crystallographically

independent molecules each located on an inversion center. Cyclotetraphosphazene ring is non planar.

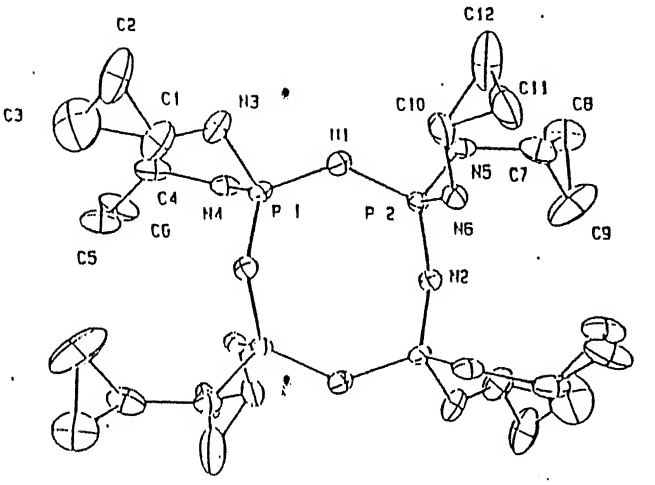

Figure 4: ORTEP diagram of OCPRA.

Polyphosphazene polymers provide excellent oppurtunity for exploring the effects of changes in side group structure on the physical property of the macromolecules. Depending on the bulkiness of the side group the skeletal flexibility changes, thus altering the glass transition temperature.

Polydichlorophosphazene prepared by the thermal polymerization of hexachlorocyclotriphosphazene, was allowed to react with cyclic amines in presence of the hydrogen chloride scavenger triethylamine to afford cyclic amino polyphosphazenes CAPCP, CAPEP and CAPRP. The characterization of these polymers was done by using a combination of multinuclear NMR, dilute solution viscosity, differential thermal analysis, differential scanning calorimetry, and thermo gravimetric analysis. All the above polymers have a small amount of residual chlorines. Attempts to substitute these by the amino groups did not succeed. In view of this the polymers tend to crosslink even in solid state over a period of time. Further, due to the presence of these residual chlorines the polymers are also susceptible to hydrolytic attack.

Dilute solution viscosity studies indicate that these polymers are of high molecular weight (CAPCP:11.8 cc/g ; CAPEP:34.7 cc/g). The ^{31}P NMR spectra of CAPCP, CAPEP and CAPRP contained a singlet resonance around 2 ppm. Similar chemical shifts are also observed for the other related derivatives. The proton NMR also consistent with the assigned structure. The glass transition temperatures are higher than other related derivatives. These side groups reduce the torsional mobility of the chain and hence the Tg is high. Among the polymers investigated in the present study Tg values increase with the bulkiness of the side group. For the polymer with small side group the Tg is lower than the bulky cyclohexylamine and cyclopentylamine substituted polymers.

Chapter 3, describes the cyclotetraphosphazene pendant monomers and their homo and copolymerization.

Three new cyclotetraphosphazene monomers TETHVB, TETQMA and TETPHS have been prepared by reacting difunctional reagents(HVB, HQMA and PHS) with octachlorocyclotetraphosphazene.

The mass spectra of these compounds were recorded both under electron impact and FAB mass conditions. In both of these methods the parent ion peak is predominantly seen at 624(TETHVB), 591(TETQMA) and 546(TETPHS), respectively. An interesting feature of the mass spectra is that while in TETQMA the first major fragmentation is by the loss of the $-COCH = CH_2$ group with almost no initial chlorine fragmentation, in the case of TETHVB and TETPHS although the initial fragmentation is due to the loss of the vinyl group there is a simultaneous two-chlorine loss.The proton NMR spectra of TETHVB, TETQMA and TETPHS show that the vinylic region is either of an ABX (TETQMA) or an (AMX) type (TETHVB, TETPHS). The ^{31}P NMR spectra of TETHVB, TETQMA and TETPHS show an AB_2X pattern with

the X region (PClR) being more upfield shifted compared to (PCl_2).

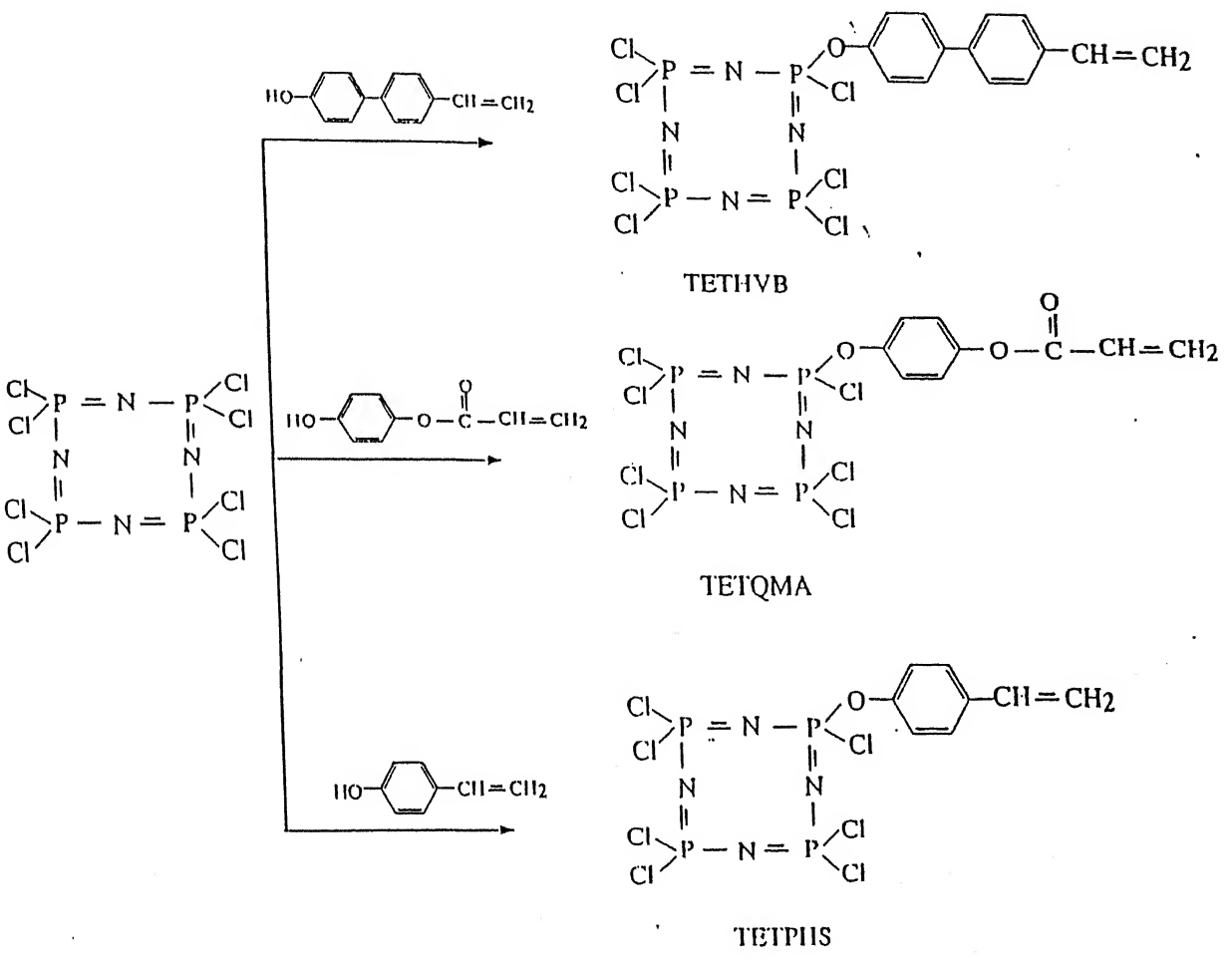

Figure 5: Synthetic Route Involved the Preparation of TETHVB, TETQMA and TETPHS.

Attempted homopolymerization of these cyclotetraphosphazene monomers by free radical methods in benzene or 1, 2 -dichloromethane for prolonged periods of time resulted in almost no polymerization. However, when the reaction medium was changed

to symmetrical tetrachloro ethane, TETHVB was found to undergo homopolymerization. The polymer is a free flowing white powder which tends to degrade upon exposure. This is presumably due to the reactivity of P-Cl bonds with moisture leading to crosslinked products as well as hydrolysis. This behaviour is in contrast to the stability of analogous homopolymer obtained from $N_3P_3Cl_5(C_{14}H_{11}O)$ which is very stable to atmosphere. This difference in behaviour can be accounted for as due to the enhanced reactivity of P-Cl bonds in cyclotetraphosphazene ring in comparison with cyclotriphosphazene ring.

The proton NMR spectrum of TETPOL 1 shows the complete absence of vinylic protons. The ^{31}P NMR of TETPOL 1 suggest the essential retention of cyclophosphazene ring skeleton in the polymer. The powder X-ray diffraction of the homopolymer indicates that it is an amorphous material. The DSC and DTA anaysis of the homo polymer indicates a glass transition around 200°C and two decompositions around 344.5°C and 587.4°C respectively.

The ^{31}P NMR of these polymers indicate the retention of cyclotetraphosphazene ring. Gel permeation chromatographic study showed that molecular weight of the styrene copolymer (HVBSTY 1) is 1 x 10^5 (Mw) with a polydispersity of 1.96. The glass transitions of the copolymers are lower than that of the homopolymer besides showing complete decomposition at 640°C.

The decomposition of TETPOL 1 in nitrogen starts at 205°C. The major fragmentation occurs at 440°C. The most important feature of this polymer is its high char yield, i.e., char yield is 35.7% in nitrogen at 850°C . Thus TETPOL 1 has a potential use as heat and fire resistant polymers. However, this polymer is less thermally stable than the one obtained from $N_3P_3Cl_5(C_{14}H_{11}O)$.

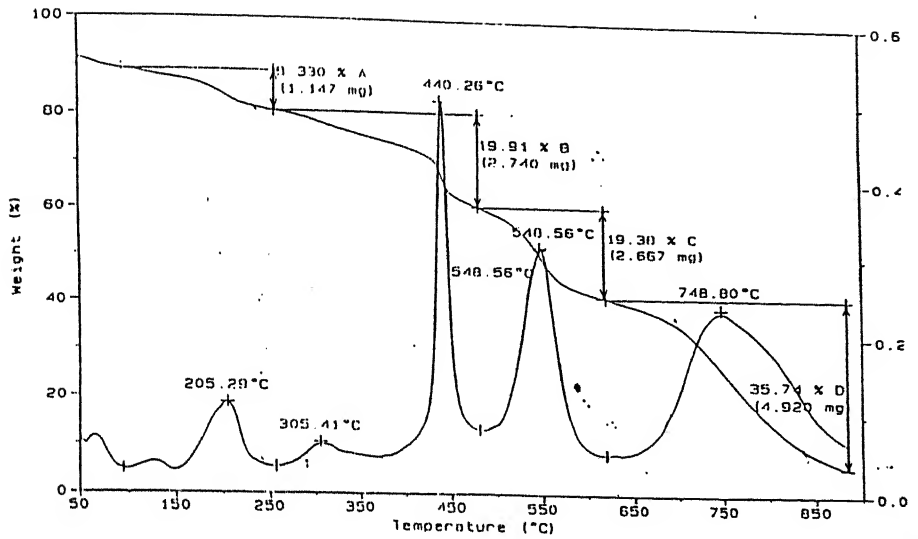

Figure 6: TGA Thermogram of TETPOL 1.

The results obtained lead to following conclusions:

1. The cyclophosphazene monomers TETHVB, TETQMA, and TETPHS all contain seven chlorines and one polymerizable organic unit. The structure of the monomers is obtained from multinuclear NMR and phosphorus-31 NMR spectra

2. All of the eight membered cyclotetraphosphazene derivatives are *extremely* sensitive to moisture and in this respect differ greatly from the analogous six membered ring $N_3P_3Cl_5(C_{14}H_{11}O)$.

3. While $N_4P_4Cl_7(C_{14}H_{11}O)$ could be homopolymerized succesfully, the other two monomers did not undergo such a reaction. There is no structural change occuring in the cyclophosphazene ring upon polymerization.

4. The homopolymer obtained from $N_4P_4Cl_7(C_{14}H_{11}O)$ is also quite reactive with ambient moisture, in complete contrast to that obtained from $N_3P_3Cl_5(C_{14}H_{11}O)$.

5. Thermal studies also indicate that the homopolymer derived from $N_4P_4Cl_7(C_{14}H_{11}O)$ is less stable(with the char yield of 35.7% at 850°C compared to the homopolymer derived from $N_3P_3Cl_5(C_{14}H_{11}O)$ (char yield 67%, 500°C).

6. $N_4P_4Cl_7(C_{14}H_{11}O)$ could also be copolymerized . All the copolymers as well as the homopolymer are flame-retardant materials.

Chapter IV describes the assembly of cyclophosphazene derivatives suitable for interaction with transition metals. All of these are pyrazolyl substituted cyclophosphazenes with the idea of involving the pyrazolyl nitrogens and the ring nitrogen of the cyclophosphazene ring in coordination. The synthesis of ligands and reaction path ways are given in the following page. The ligands have been characterized by multinuclear NMR, IR and also single crystal x-ray diffraction on HDPCTP.The Mass spectra of DIAMPZ, TETPZ and PPHVB show strong parent ion peaks.

The proton NMR spectra of the ligands are dominated by the pyrazolyl protons. The ligand DIAMPZ, PPHVB and POLYM 1 show additional features due to the amino phenyl and vinyl groups. The ^{31}P NMR of DIAMPZ and PPHVB display two resonances at 1.5 and 18.2 and at 0.4 and 3.1 respectively. The low frequency doublet is readily assigned to the PPz_2 groups since the values are very close to the singlet observed for HDPCTP.

The structure of HDPCTP as described by x-ray is shown below. The six membered ring is planar. The average P-N bond length 1.578(2)$\AA$ is comparable with P-N bond distances reported for other symmetrically substituted cyclophosphazenes.

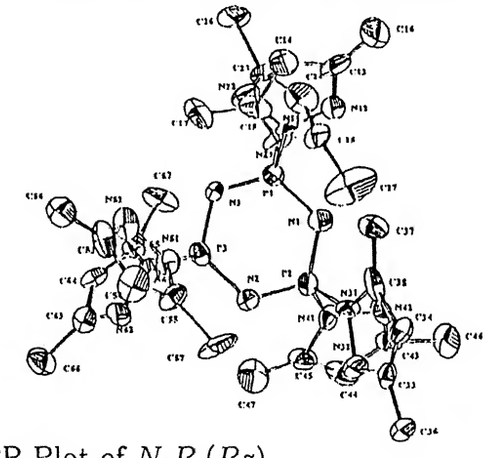

Figure 7: ORTEP Plot of $N_3P_3(Pz)_6$.

The reactions of Cu(II)X_2(X = Cl, Br) and $CoCl_2$ with the ligands TETPZ, DIAMPZ and PPHVB in dichloromethane in a 1 : 1 or 1 : 2 molar ratio yield the mono and dimetallated derivatives. Table 3 shows the physical characteristics of coordination compounds under taken in this thesis.

Table 3: Physical Characteristics of Coordination Compounds Under Taken in this Thesis.

Compound	Color	Nature	μ_{eff}(BM)	Λ_m [a]
DIAMPZ.$CuBr_2$	green	crystalline	1.62	17.49
DIAMPZ.$CoCl_2$	dark blue	crystalline	3.74	18.3
TETPZ.$CuCl_2$	light-green	crystalline	1.98	15.48
TETPZ.$CuBr_2$	brown	powder	1.71	40.90
TETPZ.$CoCl_2$	blue	crystalline	-	31.15
PPHVB.$CuCl_2$	light-green	powder	1.74	22.51
PPHVB.2$CuCl_2$	light-green	powder	1.78	25.53
PPHVB.$CuBr_2$	yellow	powder	1.91	31.05
PPHVB.2$CuBr_2$	dark-yellow	powder	2.05	14.77
POLYM 1.$CuCl_2$	light-green	powder	1.85	2.92
CAPYP.$CuCl_2$	dark-green	crystalline	1.96	32.06

[a] unit = mho cm^2 mol^{-1}

The UV-Visible spectra for PPHVB metal complexes show transition near 280nm and 360nm which can be ascribed to π_2(Pz)-Cu(II) and π_1(Pz)-Cu(II) charge transfer transitions. The band around 230nm is attributed to π-π^* intraligand transition for the bromo complexes. The EPR spectra of trigonal bipyramidal copper complexes are characterized by an axial symmetry with $g_{\|} > g_{\perp} \simeq 2.0$. The EPR spectra of PPHVB.$CuCl_2$, PPHVB.2$CuCl_2$ and PPHVB.2$CuBr_2$ are of the axial type. Attempts to confirm this by single crystal x-ray structure were not succesful as suitable crystals

could not be grown. However, these spectroscopic data are consistent with an N_3 coordination mode analogous to that of HDPCTP.

It was possible to obtain crystals of cobalt complexes of $N_3P_3(NH)_2Pz_4$. X-ray structural analysis of this compound showed that Co(II) is in trigonal bipyramidal geometry. The distrtion in geometry is clearly a result of the rigid cyclophosphazene frame work. The coordination is from two nongeminal pyrazolyl nitrogens and one cyclophosphazene ring nitrogen.

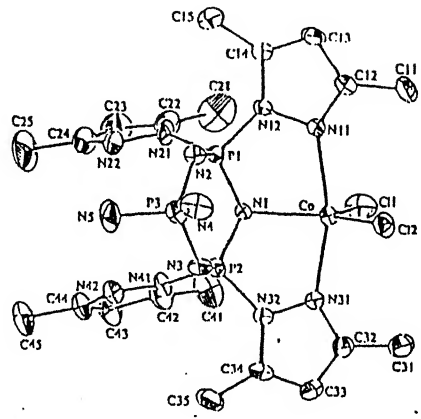

Figure 8: ORTEP Plot of $N_3P_3(NH_2)_2Pz_4.CoCl_2$.

HDPCTP is known to form metal complexes involving an unusual N_3 coordination geometry using *two* nongeminal pyrazolyl nitrogen and *one* cyclophosphazene ring nitrogen. Crystallization of TETPZ. $CuCl_2$ afforded a hydrolysed derivative. The interesting feature of this compound is, it is a homo bimetallic compound, with two coppers being present. The two coppers are bridged by a chlorine. The conformation of the cyclophosphazene ring is non planar with a saddle type conformation being adopted by the ring.

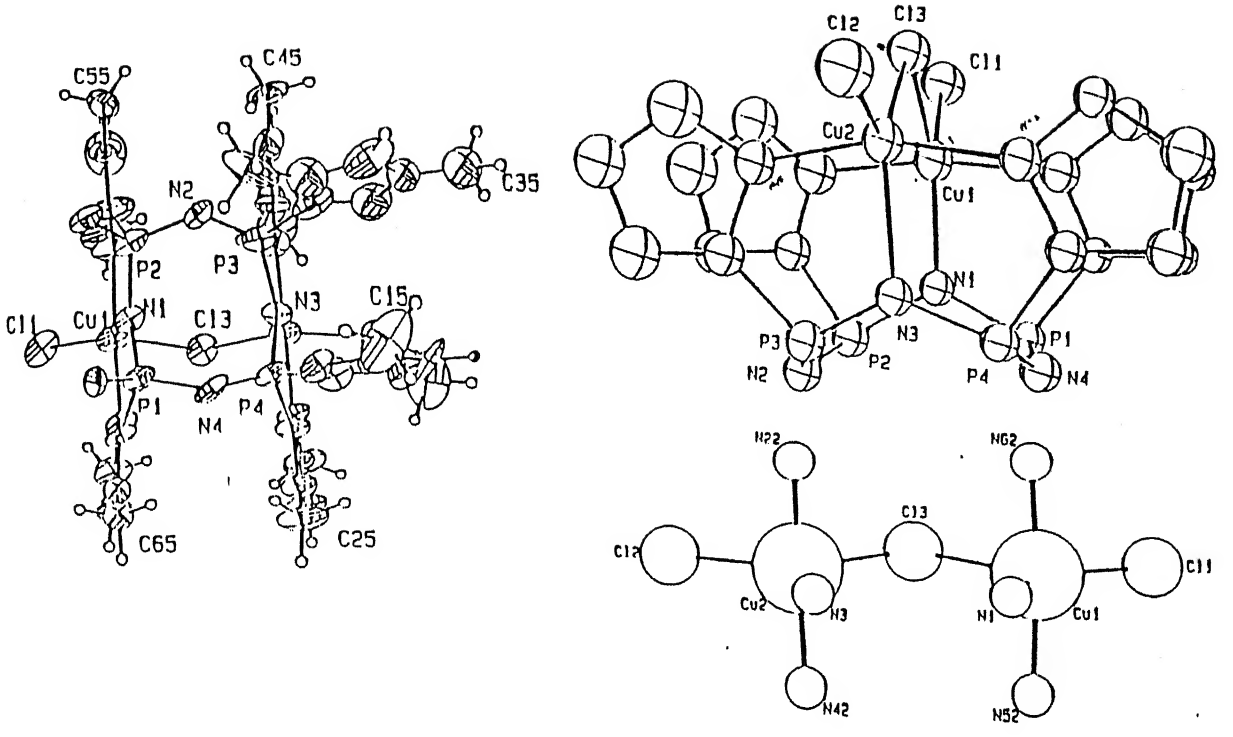

Figure 9: ORTEP Plot of Hydrolyzed Complex of TETPZ.$CuCl_2$

In contrast to the behaviour of the above ligands $N_4P_4(Pz)_8$ is extremely sensitive to hydrolysis particularly after complexation. Thus the cobalt complex of this derivative was isolated as only the pyrazolyl complex of cobalt, $CoCl_2.(Pz)_2$.

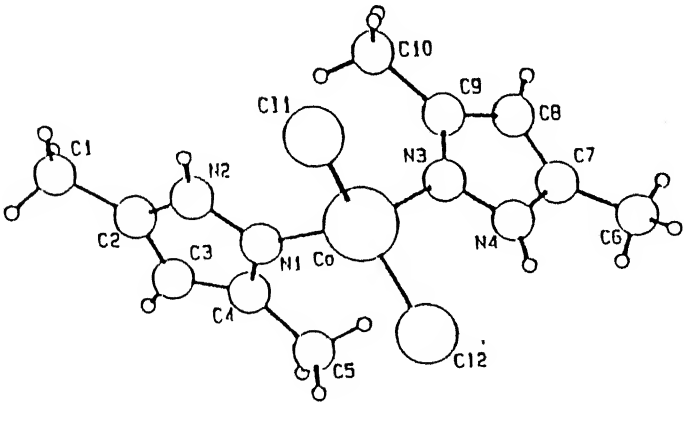

Figure 10: ORTEP Plot of Pz_2. $CoCl_2$.

The polymeric derivatives POLYM 1 and CAPYP also interact with transition metals and from a comparison of their spectroscopic data with that of the simple cyclic compounds HDPCTP, DIAMPZ and PPHVB, it is concluded that a similar coordination response as found from the cyclic analogous is obtained from these polymeric ligand. The salient features contained in this chapter can be summarized as follows.

1. Six different types of pyrazolyl substituted cyclo and polyphosphazenes capable of interacting with transition metals have been assembled. The x-ray structure of hexakis pyrazolyl cyclotriphosphazene(HDPCTP) has been carried out.

2. The ligands DIAMPZ and PPHVB interact with transition metals in a nongeminal N_3 coordination mode. This involves the use of two nongeminal pyrazolyl nitrogens and one cyclophosphazene ring nitrogen for coordination to the metal.

3. The behaviour of the eight membered cyclophosphazene TETPZ is more complex . Fully hydrolysed or partially hydrolysed derivatives are obtained after metallation.

4. The polymers POLYM 1 and CAPYP also interact with transition metals in an analogous manner as that of the simple cyclic compounds HDPCTP, DIAMPZ and PPHVB.